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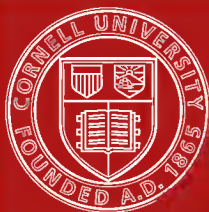
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**Introduction to chemistry.**



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INTRODUCTION TO  
CHEMISTRY

BY  
WILHELM OSTWALD

AUTHORIZED TRANSLATION BY  
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*WITH 74 FIGURES IN THE TEXT*

*FIRST EDITION*  
FIRST THOUSAND

NEW YORK  
JOHN WILEY & SONS  
LONDON: CHAPMAN & HALL, LIMITED  
1911

A.256154

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Stanhope Press  
F. H. GILSON COMPANY  
BOSTON. U.S.A.



## PREFACE.

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THE success both of the German edition and the numerous translations of the author's *Schule der Chemie* was a very welcome confirmation of the utility of the educational principles which are emphasized in that book. On the other hand, on account of the conversational form in which the work was written, it is not well adapted for use as a textbook.

In the present instance the author has attempted to write a book which will be suitable to use as a text for beginning the study of chemistry, and yet it is based upon the same general principles as those adopted in the above-mentioned work. He has attempted to make it represent the sum of his wide experience in teaching.

The greatest difficulty to overcome lies in the very large amount of material available. Most elementary textbooks attempt to cover so much ground that a student frequently gets the idea that there is nothing more to learn, and this false impression interferes greatly with his further development. If a student actually gets such an impression, it must surely be because so many isolated facts have been showered upon him that he has had no time to learn how to analyze chemical phenomena thoughtfully. In this book, however, the author has tried to show from a few simple facts how it is possible, by carefully thinking over their causes and effects, to draw many wide and deep conclusions leading to new experiments and verifications, and he has thus sought to obtain, in elementary form, a practical introduction to scientific thought from chemical instruction. In this way the student does not get the impression that his knowledge of the subject is complete because he understands the book; but, rather, he will become more and more aware of the fact that far beyond the horizon which bounds his present view stretch fields that are open to him for further investigation.

More attention than usual is paid to the development of first principles. It was rather surprising to find how far the natural development of chemical conceptions coincides, on the one hand, with their historical development, and on the other hand, with the demands of rational pedagogics. The explanation of the fundamental conceptions — *substance, solution, mixture, their properties and characteristics* — not only forms the logical basis of chemical instruction, but makes possible, as well, the systematic description of the more important chemical operations and methods of separation, which must be understood before a good knowledge of chemistry is acquired. The first third of the book contains a simple, experimental development of these general chemical relations, and the experiments chosen for illustrating and demonstrating these relations are performed, for the most part, with well-known substances. They suffice, at the same time, to make the beginner so well acquainted with such phenomena that a sound empirical basis is obtained for the systematic study of chemistry, and thereby a feeling of progress is obtained.

In this way, the student acquires a certain amount of thorough knowledge, which is more advantageous for future work than a much greater accumulation of half-digested fragments of isolated facts.

Another point of view which the author has kept in mind more than in any other of his works, is the regard for the maturity of the class of students for whom this book is intended. The ability for abstract reasoning, and the joy therein, are just dawning, whereas the interest in the diverse nature of phenomena is already well developed. For this reason the contents have been arranged as far as possible in accordance with this natural development, and abstract analyses have been carried out only as far as the connection between experiment and hypothesis is clearly discernible. This again ought to be a source of pleasure to the student, for it is unnecessary for him to proceed with a half knowledge or with a badly developed intellectual consciousness.

The subdivision of the text into sections, averaging about

a page in length, serves the same purpose. In case a further limitation of the text seems desirable, the teacher will be able to leave out certain of these sections in the instruction of the class as a whole.

It is very easy to follow the usual custom of taking mineralogy into consideration and, in the description of the chemical geological reactions which take place on the earth's surface, a welcome opportunity is found for the introduction of general considerations. On the other hand, crystallography offers certain difficulties which have been overcome in as simple a manner as possible. The customary enumeration of all the crystal forms has no educational value, although the knowledge of the elements of equal symmetry in the different forms of a system of crystals develops thought concerning spatial relations. The author feels as much justified in limiting such discussion, for the purpose of instruction, to the axes of symmetry, and leaving out the other elements of symmetry, as in the usual limitation to seven principal systems in place of the thirty-two that actually exist.

The experiments are partly new and all of them are so chosen that they can be performed easily by the beginner. Too often, in the attempt to base chemical instruction upon the results of experience, the student is called upon to witness such intricate experiments that he has neither time nor inclination to think them over carefully. Chemistry is an experimental science and it is just as much a matter of experiment as of science, which begins only with the application of experience to the formation of conceptions and conclusions. The author has tried, therefore, to give only such experiments as permit a direct scientific application, and this result is reached by the simplest conceivable means. Whenever possible, the student should perform the experiments himself. In fact, he will be able to carry out most of them at home, in case laboratory conveniences are not accessible. The experiments have been described briefly and it is intended that suggestions concerning many details not mentioned in the text will be obtained from the drawings.

### NOTE.

THE translators wish to express their obligation to Messrs. J. W. Phelan and R. E. Gegenheimer of the Massachusetts Institute of Technology for much help and friendly criticism in reading and revising the proof sheets of the English text.

W. T. H.  
R. S. W.

Boston, *March*, 1911.

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# INTRODUCTION TO CHEMISTRY

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## CHAPTER I.

### SUBSTANCES AND MIXTURES.

#### § 1. SUBSTANCES.

1. **Chemistry is the study of substances.** — Sugar, iron, sulphur, coal, etc., are substances. Substances are the material from which bodies can be made. On the other hand, water and air are substances. What is the difference between a *substance* and a *body*? Both have weight and both occupy space. In the case of a body, however, the shape is taken into consideration, whereas it is not so with a substance. A body has some particular shape and consists of some substance. Thus the knife is long and narrow and has a steel blade; steel is a substance and the knife is a body. A drop of water is globular in form and consists of water; water is the substance of the drop, and the drop itself is a spherical body. *If the question is asked: Of what does this body consist? or Of what is it made? The answer is the name of a substance.*

2. **Different bodies may consist of the same substance.** — Thus various tools for boring, cutting, punching, etc., are made of steel, and all sorts of different bodies from the large house to the small penholder and match are made of wood. *Similar bodies can consist of different substances*; thus dishes are made of clay, glass, iron, or tin, and coins consist of gold, silver, nickel, or copper.

How is the substance recognized in the body? Why is it said that this bottle is made of glass? Because it is transparent and hard, not flexible but brittle since it is broken by a knock or a blow. Moreover, the pieces of broken glass have sharp edges

by which one's finger is easily cut and if a piece of common glass is heated it is likely to crack.

All these characteristics are *properties* of glass; and glass, like any other substance, is recognized by its properties. Name the properties of steel, of sulphur, of silver, copper, and wood. Describe, or characterize, the substances which you remember by their properties.

3. **Is it possible to describe all substances?** — This task proves to be an endless one. There are countless different substances, and among them many which you yourself have never heard of but of which the plumber, the mason, or the painter knows because he uses them at his own particular trade. It is the business of the chemist to know all substances.

But is this really possible? No, for there are at present more than sixty thousand different substances known, and if the chemist should become acquainted every day with ten new substances, it would take him twenty years of three hundred working days to know them all. In the meantime, other chemists would be discovering thousands of new substances, so that the work would never end. What, then, is to be done?

Every time a chemist discovers, or makes, a new substance, he *describes its properties*. All these descriptions are collected in books (from which it is easy to find out also whether several people have described the same substance) and classified according to certain rules. When it is desired to know the properties of any particular substance, it is only necessary to look it up in some such book. Similarly, if a chemist thinks he has discovered a new substance, he examines the literature to see whether a substance with like properties has not been prepared by some one else. Only when he finds that this is not the case does he describe his substance as new and give it a correspondingly new name. Chemical literature thus replaces the human memory to a great extent, and retains all acquired knowledge independently of the life of the individual.

4. **How many properties does a substance have?** — It would be desirable to know all the properties of every substance, but this task is also an endless one because it cannot be stated just

how many properties every substance has. The properties of a substance are shown if it is *looked at, felt, smelled, tasted, bent, pressed, hammered, heated, subjected to the action of an electric current, or brought into contact with other substances.* There are, therefore, countless properties of a single substance, and it is never wholly possible to describe or recognize every property of a substance. Large volumes have been published which deal solely with the properties of a single substance such as water, iron, or sugar, and every time a new edition of such a book is printed it is necessary to mention many new properties which have been discovered since the former edition appeared.

It is therefore necessary in the course of the investigation and the description of the properties of substances to draw a line and describe only enough properties to characterize the substance. Often conditions change so that some special property which has not been previously studied becomes of importance. It is then necessary to carry out a new investigation to establish this property. If such a work has been carried out once, it suffices for all time, because *a definite substance always has definite properties no matter how or where it has been prepared.*

**5. The connection between properties.** — It is very much the same with substances as with animals and plants. Each species has its own particular properties and characteristics which are duplicated in every single individual. If it has once been established that a raven has warm, red blood it is known for all time that ravens are warm-blooded birds, and up to the present time no raven has ever been found of which this is not true. In the same way, it is well known that iron will rust, and that it will be attracted by a magnet; a piece of iron has never been found which has not shown these two properties.

With animals and plants there are always *quite a number* of characteristic properties which are all shown by a given species but are not shown in the same way by other species; and this is true of substances as well. The crow is black, has a large,

wedge-shaped bill, glistening feathers arranged in a definite manner, and a certain size and shape. When one is convinced that some of these properties are present, one may also expect to find certain other characteristics such as cleverness, cawing, etc. Similarly, in the case of a metal which rusts and is attracted by a magnet, the inference is that it will melt only at a very high temperature, that it is seven times as dense as water, that a polished surface will show a gray color and metallic luster, that it will dissolve in dilute hydrochloric acid, and, in fact, that it has all the properties of iron; these expectations will always be confirmed.

**6. How many properties characterize a substance?** — In the case of a given body it is often necessary to establish only a few properties in order to know of what substance it consists. The textbooks of chemistry, in which the different substances are described with respect to their properties, must contain, for every substance mentioned, at least enough statements concerning the properties to distinguish it with certainty from all other substances. To be sure the textbooks do not stop here, because the numerous applications of the substance in commerce, medicine, the arts, or in any field of human activity, all depend upon its properties. It is necessary, therefore, to mention all such properties and their applications. Moreover, it is not known whether a property which up to the present time has never been utilized will in the future become valuable. Hence pure science, — in contrast to applied science, which makes use of the known properties, — is constantly trying to extend as far as possible the knowledge concerning the properties of substances.

**7. The different kinds of properties.** — There are two classes of properties: (1) those which are discernible from a study of the substance itself *as it is*, and (2) those which become evident when we undertake to do something to the substance, *i.e.*, change it from its ordinary condition to particular new conditions.

Among the properties which are at once perceptible to our senses are, in the first place, those which are recognized by the

eye. In almost all cases it is the eye which first gives information concerning any substance. In this way are recognized

- (1) The Color,
- (2) The Transparency,
- (3) The Luster.

(1) We distinguish between six *principal colors*, — red, orange, yellow, green, blue, and violet. Dark orange is called brown. Then there are white, gray, and black, which are not true colors in the sense used in physics, but are nevertheless used to designate the appearance of substances.

*White*: chalk, common salt, sugar, etc.

*Gray*: lead, iron, etc.

*Black*: charcoal, asphalt, ink, etc.

*Red*: minium, cinnabar, terra cotta, etc.

*Orange and brown*: ocher, amber, lignite, etc.

*Yellow*: sulphur, gold, brass, etc.

*Green*: leaves, verdigris, emeralds, etc.

*Blue*: lapis lazuli, ice in thick pieces, etc.

*Violet*: amethysts.

The colors white, black, and brown occur most frequently in natural substances.

(2) There are three stages of *transparency*—transparent, translucent, and opaque. Glass is transparent, and it may be either colored or colorless. Thin milk is translucent, as are ground glass and oiled paper. Most substances are, however, opaque. Transparent, translucent and opaque substances, moreover, may be of any color.

(3) Finally, in the case of *luster* we distinguish the highest grade, called metallic luster, from all other ways in which substances glisten. In mineralogy, the study of substances as they occur in the earth, a distinction is made between adamantine, vitreous, greasy, silky, and pearly lusters.

Adamantine luster closely resembles metallic luster. It is shown by diamonds, which reflect a great deal of light and glisten brilliantly. Glass shows vitreous luster and fat has a greasy luster. Silky luster is produced when a number of glistening threads lie parallel to one another, each reflect-

ing the light in the shape of a line so that a peculiar shimmer is obtained. Pearly luster is caused by tiny, regular unevennesses on the shells of pearls and other bivalves, which so change the light that different colors are obtained in different directions.

A substance like chalk, which has no luster, is called lusterless or dull.

## § 2. FORMS.

A second, striking property of substances is the way they occupy space. A body is either *solid*, *liquid*, or *gaseous*, and correspondingly the substance of which it is composed is in the solid, liquid, or gaseous state.

8. **Solid bodies** are characterized by the fact that they have a definite shape which they retain unless acted upon by a force greater than gravity. Since all bodies are acted upon by gravity, the fact that a body has of itself a definite shape when not contained in a vessel, is sufficient to show that it is a solid. If it were a liquid the action of gravity would cause it to flow so that each particle would get as low as possible.

The degree of solidity varies in different substances. Lead, for example, does not have much solidity, for a rod of lead can be changed in shape and torn much more readily than a rod of iron. A distinction is made between different kinds of solidity according to the way in which it is attempted to change the shape of a solid body. Thus the resistance towards crushing, towards tearing, and towards cutting may be measured. A solid substance which can be changed readily into small, incoherent particles, for example by pounding it, is said to be *brittle*; one with the opposite qualities is said to be *tenacious*. A body which after being bent or twisted tends to revert to its original form is called *elastic*; if, on the contrary, it retains its new shape it is said to be *inelastic* or *plastic*.

All these properties are capable of precise measurement, but in elementary chemistry and mineralogy it is sufficient to estimate them roughly. Thus substances are described in general as soft or hard, as tenacious or brittle, inelastic or elastic. India rubber

is soft, tenacious, and elastic; steel is hard, tenacious, and elastic and so on.

9. **Liquids** have no form of their own, but do possess a definite volume and consequently have a definite density. In the case of liquids so little work is required to make them assume a definite form that gravity itself does this work. Liquids, therefore, assume the shape of their solid surroundings, or the vessels containing them, as far as the bottom and sides are concerned. The surface of liquid in a vessel approaches the form of a horizontal plane which is perpendicular to the direction in which gravity acts. Under these conditions the center of gravity of the liquid is placed as low as the form of the vessel permits, and thus gravity has no further influence upon the form.

There are transition stages between the liquid and solid states, for the mobility of liquids varies greatly. Benzin is more mobile than water, and the latter more than oil. Molasses, resin, and pitch are such viscous liquids that they respond but slowly to the action of gravity. This is particularly true of pitch, which may be broken quickly as if it were a solid, or by means of slow pressure it can be made to flow like a liquid. Soft and inelastic metals, such as lead, may be made to flow by means of great pressure, and threads or tubes may be pressed out.

10. **Gases** are the least conspicuous of all substances. For this reason it was a long time before the necessity was realized of describing them as a class along with the solids and liquids.

Besides the atmosphere which surrounds us and in which we live, there are many other gases with different properties. For example there is *illuminating gas*, which is so commonly used as a source of light and heat, *hydrogen gas* with which balloons are filled, and *carbonic-acid gas*, which is used in soda water and in chemical fire extinguishers. All these gases are colorless, although other gases will be mentioned which have a perceptible color. It is likewise true that there are more colorless liquids than colored ones.

Gases have neither a definite form nor a definite volume, but they completely fill any vessel in which they are placed.

Thereby they exert a certain amount of pressure upon the walls of the vessel containing them, and the pressure can be made larger or smaller. This pressure depends upon the amount of the gas that is contained in the vessel, for it increases in proportion to the amount of gas that is introduced. This is evident on pumping up the tire of a bicycle; the more air pumped in, the harder the tire becomes.

We live within an ocean of air, just as fish live in an ocean of water; and the air fills not only our lungs and the other cavities of the body but is also contained in every open vessel. If we say that a bottle is empty we mean that it contains nothing but air. *Something* is actually present in the bottle, as is evident from the fact that if it is inverted and placed in water, the latter penetrates only a little way. If the bottle is then turned right side up again, while completely immersed, air bubbles will escape through the water and the bottle will fill with water. From these experiments it is evident that the air is much less dense than water. The difference, in fact, is very great; water is, in round numbers, twelve hundred times as dense as the air which surrounds us. In other words, a gram of air under ordinary conditions will occupy a volume of about 1200 cc., or 1.2 liters. The density of air and that of all other gases vary greatly with the pressure.

Since gases fill all vessels, and since, moreover, their density is so slight, they cannot usually be seen, especially if colorless. Their presence is most readily recognized when they are entirely or partly surrounded by water. If the bottom of a muddy pond be stirred with a stick, bubbles of gas will usually escape upward through the water. This gas may be collected by filling a glass cylinder with water and inverting it over the escaping bubbles.

### § 3. WEIGHT.

**11. All bodies have weight.** — Weight represents the force with which the body tends to fall, or to approach the center of the earth. The existence of weight is recognized if the attempt is made to lift a body; a certain amount of work is required, which of course varies greatly with different bodies.



A feather is so light that it is hard to realize that it actually has weight; on the other hand, a boulder is so heavy that we do not attempt to lift it because we know that it is beyond our power. In this way we learn to recognize that bodies have different weights and we learn to estimate whether two bodies have the same or different weights. Such estimations are always more or less indefinite and inaccurate.

Accurate measurements of weight are made with a balance (Fig. 1). This consists of a lever which usually has two arms of equal length. For some purposes balances with unequal arms are used and there are even balances with only one

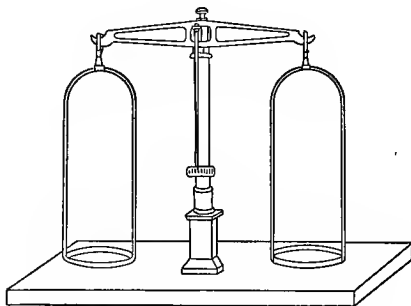


Fig. 1.

arm. If different bodies are placed in the scale pans which are suspended from the ends of the arms, usually one pan sinks and the other rises. In that case the body in the scale pan which drops is said to have the greater weight.

If, however, the balance arm is not deflected in either direction, the bodies in the different scale pans are said to be of equal weight, and the balance is in equilibrium.

Physics teaches that the force of gravity, or the absolute weight of bodies, varies at different places on the earth's surface and at different altitudes; but two bodies which have the same weight at any place will also be equally heavy at any other place. In other words, the absolute weight of every body changes at different places in the same proportion. If a balance is in equi-

librium at any place, it will remain in equilibrium at any other place. If, therefore, weights are compared with one another by means of a balance, it is not at all necessary to take the absolute weight into consideration.

**12. The unit of weight.** — To determine the weight of a body so that it will be known everywhere what is meant, a standard or *normal* weight has been chosen arbitrarily. This is the weight of a certain piece of platinum, which is one of the most unchangeable substances. This piece of metal is preserved with great care in Paris and is called the *standard kilogram*. Furthermore, there have been prepared about twenty other weights as nearly like it as possible, and which have been very carefully compared with the standard kilogram; these are preserved at the capitals of the different civilized countries. Other kilogram weights are compared with them and are kept in the various standardizing bureaus, and in the offices of the makers of weights, etc., so that they serve as a basis for all determinations of weight. The abbreviation kg. is commonly used for kilogram.

The thousandth part of a kilogram is called a gram, abbreviated g. This weight is the *unit* which is commonly used in science. There are other units of weight commonly used in commerce, but none of them is so convenient as the gram, which is the basis of the so-called *metric system*. The thousandth part of a gram is called a milligram, mg., and a metric ton is equivalent to 1000 kilograms or about 2205 English pounds.

The other names such as decagram-10 g., hectogram-100 g., decigram-0.1 g., and centigram-0.02 g., are not used very much; it is easier to say 10 g. than 1 decagram.

To determine the weight of a given body, it is placed upon the left-hand pan of a balance and in the opposite pan enough weights are placed to restore equilibrium. Then the weights used are counted, and the sum is the weight of the body.

SETS OF WEIGHTS, Fig. 2, are readily obtainable. The weights in such a set are always so chosen that any weight between the smallest and largest can be obtained readily.

The state of equilibrium is recognized not by the balance being at rest but by the fact that when the beam is made

to rest upon the central knife-edge the pointer will swing the same number of divisions to the left as to the right of the zero point, on the scale at the bottom.

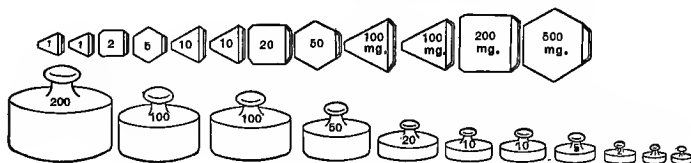


Fig. 2.

The student should weigh a number of bodies in order to gain practice in weighing. The weights should always be kept in proper order in the box, and should be used in regular order, taking a weight off the pan if it proves too heavy, and adding another weight if it proves too light. After recording the weight of a body in the laboratory notebook, the weight should be checked by adding up a second time.

If it is desired to know the weight of a liquid, a flask is first weighed empty, then the liquid is added, and a second weighing made. The difference between the two weights represents the weight of the liquid. If the weight of the flask used is determined once for all, then the weight of liquid in it can be determined readily at any time. In such a case it is customary to call the exact weight of the empty vessel the *tare*, and the vessel is said to be *tared*. Often the tare consists not of weights but of a piece of metal, or shot, or anything that is known to balance the empty vessel.

**13. The weight of air.** — Although the fact that solids and liquids have weight is a matter of common, everyday experience, it was a long time before people realized that air and other gases also have weight. This may be proved by the following experiment.

Take a large flask with thick walls, and fasten in the neck of the flask a rubber stopper into which is fitted a glass tube with stopcock. Tare the flask. Then, by means of a bicycle pump,

introduce a little more air into the flask; close the stopcock, and again weigh. The second weight will be found a little larger than the first, the gain in weight depending upon the size of the flask and the amount of air which has been introduced. Now open the stopcock and note that air escapes and the flask becomes as light as it was originally.

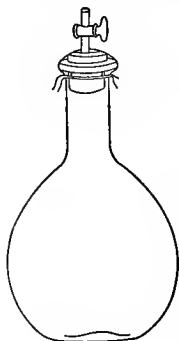


Fig. 3.

Similarly, the flask can be made *lighter* if the air is partially removed from it by means of a vacuum pump. In this case, if the stopcock is subsequently opened, air rushes into the flask, and there is a gain in weight, so that the original tare is finally obtained.

It is true, to be sure, that the flask is lifted somewhat by the surrounding air and appears, in accordance with the Principle of Archimedes, as much lighter as the weight of the displaced air. Inasmuch as this diminution in weight is the same in the case of all the above weighings, it has no influence upon the observed differences in the experiments. If the weighings were made in a vacuum, a very inconvenient though possible procedure, it would be necessary to add in each case a small weight equal to the weight of the displaced air, but the differences in weight as found above would be the same.

#### § 4. DENSITY.

In our daily life, and in science, there are two other quantities to measure besides weight, namely *time* and *space*. Although we shall find in the study of chemistry that the former comes less frequently into consideration, the latter is of great significance, especially in connection with weights.

**14. Unit of Space.** — Just as in the case of weights, the unit used for measuring space is chosen arbitrarily and consists of a platinum rod of a specified cross-section which is preserved at Paris with the same precautions as taken in the case of the standard kilogram; it is called the *standard meter*. The unit of length is the distance between two marks near the ends of

the rod. Copies of this meter have been made and serve for standards in the different countries which have adopted it as a unit.

The hundredth part of a meter, abbreviated m., is called a centimeter, cm., and this is the usual unit in chemical measurements. A decimeter = 10 cm. and a millimeter = 0.1 cm. 1000 meters are called a kilometer; it is about five-eighths of an English mile.

The units of surface and of volume are derived from this unit of length; the square of which each side measures 1 cm. is the scientific unit of surface and is called the square centimeter, sq. cm.; the cube of which each edge measures 1 cm. is the unit of volume and is called the cubic centimeter, cc.

The units of weight and of volume are so related to one another that the weight of 1 cc. of water is 1 g. Since the temperature of water influences the volume which it occupies, this last statement is true only at the temperature  $+4^{\circ}$  C., at which temperature the density of water is greatest. Similarly the weight of a cubic decimeter of water at this temperature is 1000 g., or 1 kg. A cubic meter of water weighs a metric ton.

**15. Density.** — Every body has a definite weight; on the other hand it cannot be said that every substance has a definite weight, for a large piece of iron weighs more than a small one, and yet both pieces are composed of the same substance, iron. It is, nevertheless, true that the words *light* and *heavy* can be applied to substances, for we say lead is heavy and cork is light, although a little shot of lead does not weigh much, whereas a bale of cork, as it is transported, is fairly heavy. Evidently, then, these words indicate a property whereby the weight of a body composed of a given substance is compared with the space which it occupies. Pieces of lead and of cork which are of equal size are of quite different weights; the cork is much lighter. The property of substances which governs these conditions is known as *density* or *specific gravity*.

*The weight in grams of 1 cc. of a substance is its density.* As the weight of a piece of substance twice as large is also twice as great, it follows that the relation between weight and

volume in the case of a given substance is always the same; so that the density,  $D$ , of a substance is its weight,  $G$ , divided by the volume,  $V$ , that it occupies; or,  $D = \frac{G}{V}$ . To find the density of a substance, therefore, it is necessary to weigh it and to determine its volume.

We have already seen how the weight is obtained. The space that a body occupies can be readily computed if it has a definite geometric shape; its dimensions are measured by the compass and rule and the computation is carried out according to the rules of geometry.

If  $l$  is the length of a side of a cube, then  $l^3$  is its volume.

If  $d$  is the diameter of a sphere, then its volume is  $\frac{1}{6} \pi d^3 = 0.524 d^3$ .

If  $a$ ,  $b$ , and  $c$  are three adjacent sides of a right-angled parallelepiped, its volume is  $abc$ .

If  $d$  is the diameter of the base and  $h$  the height of a cylinder, then its volume is  $\frac{1}{4} \pi \cdot d \cdot h = 0.785 d^2 \cdot h$ .

If the body, on the other hand, does not have any definite geometric form, its volume must be determined in some other way. A simple method is to take a cylinder, the

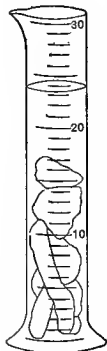


Fig. 4.

capacity of which is graduated in cubic centimeters and their tenths by lines etched in the outer wall (Fig. 4). Enough of some liquid to cover the solid entirely is placed in the graduated cylinder (alcohol or benzine is better than water, as these liquids wet the surface of solids more readily and are not so likely to allow air bubbles to remain adhering to the solid) and the volume of the liquid is read before and after introducing a weighed amount of the solid substance. The difference in the two readings gives the volume of the substance. The substance may be introduced in one piece or in several pieces. The liquid must not dissolve the substance or act upon

it in any way. It serves merely to fill up the spaces in the cylinder so that the latter is entirely filled to the surface of the liquid.

There are many other methods for determining densities, as will be seen by consulting any textbook on Physics.

**16. Densities of solids.** — The following are the densities of certain common substances.

Aluminium.....	2.7	Glass.....	2.5	Saltpeter.....	2.09
Ammonium chloride	1.52	Gold.....	19.2	Silver.....	10.5
Brass.....	8.4	Iron.....	7.8	Sulphur.....	2.0
Calcite.....	2.71	Lead.....	11.3	Sugar.....	1.59
Copper.....	8.9	Magnesium...	1.7	Table salt.....	2.16
Cork.....	0.2	Platinum.....	21.4	Zinc.....	7.1
Gypsum.....	2.32	Quartz.....	2.65		

**17. The density of liquids** is much easier to measure than that of solids; because of their property of assuming the shapes of the vessels containing them, they can be made to occupy a space of known size. If then the weight of such an amount of liquid is determined, the necessary data are known from which the density can be computed.

To determine the capacity of a vessel which is to be used for measuring the density of liquids, advantage is taken of the fact that 1 g. of water at 4° C. occupies 1 cc. of space. If the vessel contains  $N$  g. of water, its capacity is  $N$  cc.; if  $P$  g. of a liquid are contained in this space, then the density of the liquid

$$\text{is } \frac{P}{N}.$$

In carrying out such experiments, it is necessary that the vessel used should be filled to the same extent in every case. This is easily accomplished, for example, by means of a bottle with ground-glass stopper; the latter has on one side a fine groove through which the excess of the liquid escapes. Practically the same end is accomplished by marking a horizontal line around the neck of a flask, to denote a definite cubic content. Then, in the case of liquids which wet glass, the flask is filled with liquid until the lowest part of the rounded surface (called the meniscus) just touches this line (Fig. 5). Liquids which do not wet glass have a convex meniscus, and when the meniscus is on the level with the mark the volume is less than if the meniscus were concave (Fig. 6). For such liquids of which mercury is a common example, the bottle with the stopper should be used,

or the difference in volume caused by the convex meniscus is computed and the corresponding correction applied.

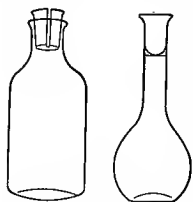


Fig. 5.

Bottles, or flasks, that are used for determining densities of liquids are called *pycnometers*. For convenience in computation, and especially with pycnometers marked by a line on the neck, the capacity chosen is made to be a round number

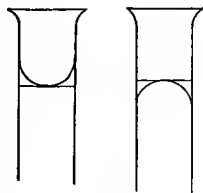


Fig. 6.

of cubic centimeters, *e.g.*, 10 or 100 cc. The weight of liquid in the pycnometer is obtained by deducting the weight of the empty vessel from the weight when filled with the given liquid. The former weight is always the same, so that it is determined once for all; in accordance with commercial usage, this weight is known as the tare (*cf.* p. 11). If  $S$  is the weight of the filled vessel, and  $T$  the tare of the pycnometer, then  $S - T$  is the weight of the liquid and its density is  $D = \frac{S - T}{V}$ , where  $V$  is the volume or weight of the water which the pycnometer will hold; or if  $W$  is the weight of the pycnometer filled with water, the formula for the density becomes  $D = \frac{S - T}{W - T}$ . All the values in this last equation can be determined directly, and in a given case it is only necessary to substitute the proper numbers in this formula.

The density of mercury is particularly important because this metal is so frequently used in physical and chemical apparatus. It is at once evident, upon lifting a bottle of mercury, that the liquid is very dense. It is easy to spill some of the liquid, on account of its being so heavy, hence, in order not to lose the valuable material, it is always well to handle it over a tray with raised edges so that the drops can be collected in case any spills. The exact density of mercury is 13.596 at 0°.

The following table gives the densities of well-known and much-used liquids. It may be mentioned that the density of



all these liquids varies with the temperature; they expand and become less dense on being heated. The values given hold true, unless otherwise stated, for the ordinary room temperature of 18° (64.5° F.).

### 18. Density of Common Liquids.

Water at 0°	0.99987
4°	1.00000
10°	0.99973
18°	0.99862
20°	0.99823
30°	0.99567
50°	0.98807
100°	0.95838
Ether	0.717
Alcohol	0.7911
Benzene	0.881
Chloroform	1.493
Acetic Acid	1.053
Glycerol	1.26
Olive Oil	0.91
Petroleum	0.8
Carbon Disulphide	1.265
Turpentine	0.87
Mercury at 0°	13.596
Mercury at 18°	13.552

19. The numerical values of properties. — Density is a property of substances just as much as color or luster. It is possible to estimate it approximately by holding some of the substance in the hand, lifting it, and comparing its weight with the space that it occupies. This, however, is not very definite and enables one merely to detect marked differences. For this reason it has become necessary to replace the direct judgment of the hand and eye with the balance, meter stick, and the graduated cylinder. The property in question can be described much more precisely by means of a number than by a word. Discernible properties such as color and luster have to be described in words, and this is always more or less unsatisfactory. Thus the pigments minium, cinnabar, carmine, red ocher, and rouge are described as red, and yet the colors of these substances are different, as can be seen at a glance.

In science, it is the constant endeavor to give, as far as possible, numerical values for all properties, because such values are influenced to a far less degree by the accidental personal judgment and by the skill or experience of the observer, and at the same time they permit much more diversified and graded distinction. Density is such a measurable property. It has been found that in the case of a definite substance the density always has the same value. Thus, for example, the density of water at  $+4^{\circ}$  C. is always unity. No matter what the source of the water may be, provided it is pure, its density is always the same.

It has also been found that the density of lead is always 11.3, for 1 cc. of lead always has that weight. Lead is obtained in different places and by various methods from all sorts of ores, but a piece of the pure metal always weighs 11.3 times as many grams as the number of cubic centimeters of space that it occupies.

Thus, conversely, density is a property which may be used for identifying substances. In the case of an unknown substance found in the earth, its density may be determined and then the tables searched until a substance is found of exactly this density. Then the other properties are compared for the sake of certainty.

## § 5. HOMOGENEOUS SUBSTANCES AND MIXTURES.

**20. Mixtures.** — It is possible to classify substances with regard to the color, transparency, and luster only when every part of the substance has exactly the same properties as all other parts. Many substances, however, are composed of parts having different properties. In a sausage it is possible to distinguish the white fat from the red meat, so that it cannot be said that a sausage is composed of a substance which is either white or red. A sausage consists in fact, not of one substance but of two — fat and red meat. Furthermore, in reality these are not the only substances present in a sausage, for it is possible to detect black grains of pepper and perhaps other substances. Such a body, composed of several substances, is termed a *mixture*.

Mixtures are formed when two or more substances are brought together to make a body. It is not necessary, however, to make

mixtures, for they frequently occur in nature. Thus it is evident, from a careful examination, that granite is a mixture of different substances; it is possible to distinguish in the rock, grains of different colors, different luster, and different degrees of hardness.

The properties of a mixture depend entirely upon the properties of the different substances present, and upon the relative amount of each substance. Thus, for example, if sand is mixed with a little water, the resulting mixture behaves almost like pure sand; it is moist sand. If, however, a much larger amount of water is added, a paste is obtained which can be made to flow. Finally, a very little sand in a great deal of water gives a turbid water which has nearly the same properties as pure water.

Similarly, powdered charcoal gives a black mixture with chalk, if considerable of the former substance and less of the latter is taken. A gray mixture is obtained if the proportion of white chalk is increased somewhat, and the mixture becomes whiter in proportion as the ratio of chalk to charcoal increases.

The properties of mixtures are intermediate between those of their individual constituents, and, by changing the proportions of the constituents, the properties may be changed to approach more nearly those of any one of the individual constituents.

**21. The recognition of mixtures.** — It is not always possible to recognize at once whether a body consists of a single substance or of a mixture. As long as the particles are large enough to be recognized, it is a simple matter provided the different substances in the mixture have a different appearance (*e.g.*, different color). Often, however, the particles are so small that they cannot be seen with the naked eye. In this case the body is examined with a magnifying lens or with a microscope.

A turbid, or opaque, appearance is an indication of a mixture. White powders usually consist of substances that are colorless and transparent when in a pure, coherent state. The individual particles of such a powder are separated from one another by air, and it is this mixture of the substance with the air that is white and opaque.<sup>1</sup> In the same way clear water becomes opaque

<sup>1</sup>The opacity is really caused by the multitude of small surfaces which reflect the light in all directions.

when mixed with air, as in the foam made by a breaking wave or by the propeller of a steamship. Soapsuds, likewise, consist of a clear liquid mixed with air. If a clear crystal of calcite or Glauber's salt is pulverized, a white, opaque powder is obtained.

Since from any two substances innumerable mixtures may be prepared by mixing in different proportions, it is evident why it is that we meet with many more mixtures than homogeneous substances. When mixtures are made in the same proportions, the resulting properties are the same. It makes no difference whether 2 g. of charcoal powder are mixed with 20 g. of chalk, or 3 g. charcoal with 30 g. chalk; the gray color and other properties remain the same as long as the mixture is in the proportion 1 : 10.

The properties of a mixture, then, do not depend upon the absolute amounts of the constituents but upon the ratio of their weights.

If different substances are well mixed with one another in a mortar or in a mixing machine, the resulting mixtures are uniform, and such mixing never causes a separation into the constituents. Thus the druggist mixes white powders, the painter obtains intermediate tones from pure colors, and the cook mixes oil and vinegar for salads. To prepare a uniform mixture it is only necessary to continue the process of mixing for a sufficiently long time.

**22. Separation of mixtures.** — Whether a mixture separates of itself into the constituents, either rapidly, slowly, or not at all, depends upon the nature of the mixture itself. If one constituent of the mixture is liquid or gaseous the separation usually takes place readily and quickly, and in such cases it is often hard to prepare a uniform mixture. On the other hand mixtures of solids remain the same if they are kept at rest; it requires a certain amount of work to separate such mixtures into the constituents.

All mixtures can be resolved into their constituents. By powdering a piece of granite, and working with the aid of a lens, it is possible to sort out and separate the white quartz, the pink feldspar, and the glistening mica. In this way little heaps of each constituent present can be prepared, each heap containing a

pure substance which is no longer a mixture, and the number of heaps will correspond to the number of substances in the mixture. Thus if all mixtures were separated into their constituents by some such physical process, nothing would remain but pure substances.

Separation as above, by means of *sorting*, is possible when the individual components of the mixture can be distinguished by their appearance. The process is a feasible one, however, only when the individual particles of the pure substances are relatively large. It is an easy matter to sort out a mixture of apples and pears. In the case of a mixture of oats and barley, however, the operation would be more tedious and more difficult. It would be practically impossible to effect in this way a separation of a mixture which was in the form of a fine powder.

**23. Sifting and elutriation.** — When a separation cannot be effected by sorting, some other means must be employed. The simplest is *sifting*, a process which may be applied when the parts to be separated are of different size. Thus gravel is separated from fine sand by throwing the earth against a wire screen held in an inclined position. The sand passes through the meshes, leaving the gravel behind. Similarly screens, or sieves, are used in the country to separate the chaff from the larger grains; and likewise the miller separates the flour from the bran. According to the size of the flour particles to be separated, the meshes of the screen or sieve are made close together or wide apart. Screening, sifting, straining, and bolting are nearly synonymous terms and all represent the same kind of process.

Another process is that of *elutriation*, which depends upon the fact that when a powder comes in contact with a stream of water, the lighter particles will float off with the water, while the heavier ones sink to the bottom and remain behind. Inasmuch as the valuable ores from which the metals are obtained are usually very much denser than the worthless rocks associated with them, and which constitute the so-called "gangue," ores are concentrated by powdering, stirring them up with water, and letting the lighter particles float off. In such a way gold is "washed" or "panned" from the sand in which it occurs.

24. **Other processes of separating.** — Still another process depends upon the fact that when a mixture is placed in a liquid which is denser than one constituent in the mixture but less dense than another, the former will float on top of the liquid and the latter sink to the bottom. The two portions may then be separated at will. It is convenient to use for this purpose a vessel such as is shown in Fig. 7; after the separation has been effected the stopper is inserted, to keep back the bottom portion while the liquid is poured off.

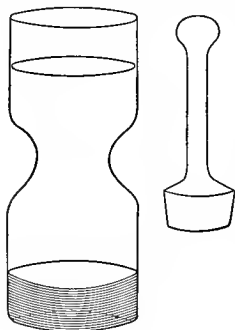


Fig. 7.

Other properties than the density may be utilized for separating a mixture into its components. Thus, for example, in a mixture of sand and iron filings, the latter may be withdrawn by the aid of a magnet. Iron ores consisting of a mixture of iron oxide and gangue (clay, sand, etc.) may be concentrated in a similar manner. For this purpose the ores are caused to fall near the poles of a strong electro-

magnet, in such a way that the more magnetic portions are drawn to one side, whereas the impurities fall straight down.

It is evident that all these processes of separating depend upon the fact that certain portions of a mixture behave differently under certain influences, and may thereby be separated in space from the other portions. Since the constituents of a mixture have different properties (or otherwise it would not be a mixture but a homogeneous substance) it is always fundamentally possible to separate a mixture into its constituents, and in every case it is merely a practical question of deciding which method will give the quickest and best results.

25. **Separating a solid from a liquid.** — The chemist frequently has occasion to separate a solid substance from a liquid one, and this is effected principally by two methods — *settling* and *filtering*. The former process can be used when the density of the liquid is less than that of the solid, as is usually the case. The mixture is simply allowed to stand, and then, by the action of gravity,

the solid particles after a time collect on the bottom of the vessel. By carefully pouring, or by means of a pipette (Fig. 8), the greater part of the liquid can be collected by itself, although the solid usually remains wet with liquid; this last portion of liquid cannot be removed completely in this way. If it is desired to remove as much as possible of this adhering liquid, the paste is placed in a bag made of porous material, and the liquid is squeezed out by means of a press. Still better is the application of centrifugal force, which consists in making the mixture revolve rapidly in a circular orbit by means of a suitable apparatus. Hereby every particle is subjected to the action of a force which is similar to gravity only much stronger, so that the liquid is thrown out, while the solid is

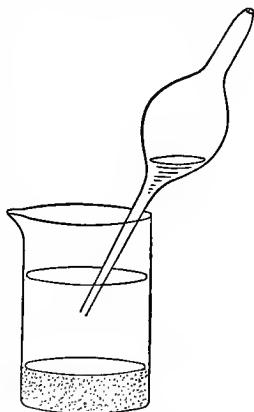


Fig. 8.

kept back by means of a strainer or something similar. Although the separation of solid and liquid is much more complete when effected in this way, it is still by no means perfect. If it is necessary to remove the last traces of liquid, recourse must be had to another process, namely to evaporation or to the use of solvents. These operations will be discussed subsequently.

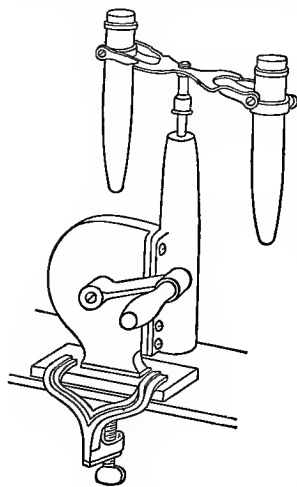


Fig. 9.

Centrifuges (Fig. 9), also based upon the action of centrifugal force, are used to make fine precipitates settle more quickly and more completely than they would by the action of gravity. The liquid is placed in the apparatus, which in this case contains no strainer, and by very rapid rotation the heavier solid material is thrown farthest away from the center.

26. **Filtration.** — In presses and in centrifugal machines a process is employed, already mentioned above, called *filtering*. This is really based upon the same idea as the process of sifting (p. 21), only it permits of a far wider application, since all liquids behave like extremely fine powders and will pass through the very finest strainers.

As strainer, a fabric is usually used for work carried out on a large scale, but in the laboratory it is almost always a *filter paper*. This is a pure paper, the fibers of which, unlike writing paper for example, have not been filled up with sizing. Such sizing is necessary in writing paper, as otherwise the ink will penetrate through the paper and spread; blotting paper on the other hand contains no sizing because it is intended to absorb ink. Thus, in the case of the unsized filter paper, the water, or other liquid, penetrates as through a very fine strainer, but any solid particles are kept back.

A disk of filter paper is folded twice so that the paper is divided into quadrants, and then the paper is opened to form a

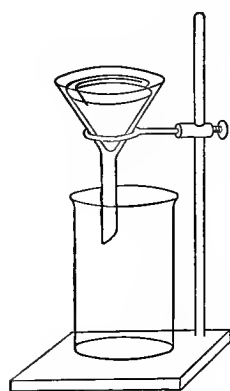


Fig. 10.

hollow cone with three thicknesses of paper on one side and one on the other. This hollow cone is placed in a glass funnel of  $60^\circ$  (Fig. 10) and moistened with a little water. Then the paper is made to fit tightly against the sides of the funnel, changing the folds a little if necessary. A beaker is placed beneath the stem of the funnel, and on pouring a turbid liquid upon the filter, a clear liquid called the *filtrate* runs through, leaving the solid behind on the filter. If it is desired merely to obtain the liquid free from the particles of solid, a so-called "plaited" filter is often

used, which is folded into sixteen or thirty-two divisions, and affords a more rapid filtration. In filtering, it frequently happens that the first portions of liquid come through turbid because the pores of the paper are a little too large. During the filtering, however, the fibers swell somewhat and, more-



over, the interspaces become clogged with some of the solid; after the filtrate once comes through clear, it is collected by itself and the turbid portion is poured through again. If it is desired to obtain the solid substance from a mixture of solid and liquid, the smooth filter (*i.e.*, the one folded into quadrants) is used, and it is frequently necessary to remove all of the original liquid. This is effected by *washing the residue*, which consists of pouring another liquid upon the filter in the funnel and letting it run through until all the original liquid has been replaced. Frequently the original liquid is a solution, and pure water is used for washing. All sorts of other liquids are employed for the same purpose. Simply filling the funnel with liquid once and then allowing it to run through never suffices, but the washing must be continued for a longer or shorter period according to the desired purity of the solid.

It is often well to combine the processes of settling and filtering. The solid is allowed to settle, the clear liquid is poured through a filter (decanted), the solid is mixed with more liquid and again allowed to settle, etc. This is called *washing by decantation*.

**27. Mixtures of two liquids** which are insoluble in one another can be separated by means of gravity if the density of the liquids is different. Two layers of liquid are then formed, with the denser liquid at the bottom. These are separated conveniently by means of a so-called "separatory funnel." This is a funnel (Fig. 11) which can be closed at the top by means of a ground-glass stopper, and is fitted, where it joins the stem, with a stopcock. The latter is closed and the mixture of liquids poured into the funnel. After the two layers have formed, the stopcock is cautiously opened and the lower liquid is allowed to run out, but the stopcock is closed as soon as the upper liquid reaches it.

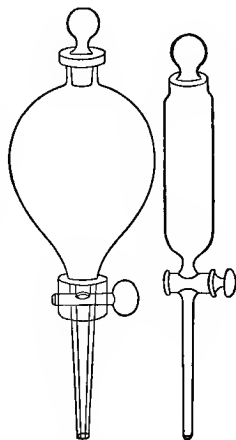


Fig. 11.

as the upper liquid

If one liquid forms very fine drops in the other, it frequently takes a long time to settle out of itself. Here also the application of centrifugal force aids greatly in effecting the separation. For example, milk is an emulsion of tiny fat globules in an aqueous liquid. On allowing milk to stand, the lighter butter-fat gradually collects on top; but by means of centrifugal force the separation can be made to take place quickly and much more completely. Thus, in the creamery, a heavy cream is obtained from milk by means of a "separator" in a much shorter time than by the old-fashioned method of "setting and skimming."

**28. The separation of gases from solids or liquids** is a very simple matter, so that it is seldom necessary to make use of any special form of apparatus. The difference in density is so great, in this case, that the separation takes place quickly of itself. Only when the particles of solid or liquid are very small (as in dust or fog) does the separation take place so slowly that an acceleration seems desirable.

This is effected, in such cases, by means of filtration, using as a rule a wad of cotton, or some such material, which will hold back the very fine particles of dust as the gas passes through it.

On a large scale, where such a method of filtering would require too much time, the dusty air is made to revolve very quickly within a cylinder, or drum, whereby the dust is thrown off by means of centrifugal force and is collected as it falls on the outside.

## CHAPTER II.

### PHYSICAL TRANSFORMATIONS.

#### § 6. FUSION AND SOLIDIFICATION.

**29. Fusion.** — A solid substance does not remain a solid under all conditions, but on being heated it can be transformed to a liquid. This fact is apparent every winter. If the temperature is below  $0^{\circ}$  C., solid ice and snow lie on the streets, fields, and brooks. As soon as the temperature has risen above the freezing point, the solid ice is transformed again into liquid water.<sup>1</sup> Then the streets which were dry become wet and the rigid covering on the river is set in motion.

All other solids behave like ice in this respect, except that the temperature at which the *melting* or *fusion* takes place varies greatly. Wax melts in hot water, sulphur must be heated a little hotter, lead melts readily in a flame, but copper and iron do not, although even these metals can be liquefied by still more heat. Carbon will not melt in any furnace, but only in the electric arc. Every substance, however, can be liquefied eventually, for it is possible to reach the required temperature.

Conversely, it is possible by cooling to transform every liquid into a solid. Liquid iron solidifies at about  $1400^{\circ}$  C., water at  $0^{\circ}$ , and alcohol at  $-112.3^{\circ}$  C.

Whether a substance is solid or liquid under ordinary conditions depends upon the location of the melting or solidification point. If it lies above about  $15^{\circ}$  C., we know it as a solid; if below, as a liquid. If we were living at a temperature of about  $500^{\circ}$ , our world would have a quite different appearance inas-

<sup>1</sup> The melting of the ice requires some time, but the temperature of the water in contact with the ice remains at the freezing point until all the ice is melted.

much as many substances which we now know as solids would then be kept in vessels as liquids.

**30. Forms of matter.** — Strictly speaking, water and ice are two different substances because they have quite different properties. The one is liquid, the other solid; the density of ice is about one-ninth less than that of water, for it floats upon the latter and immediately rises if it is pushed beneath the surface; it does not conduct electricity, whereas water does, etc. Similarly, there is a difference in properties between solid and liquid wax, solid and liquid copper, etc.

It is customary, however, to designate these two substances which are formed from one another by fusion or solidification caused by a change in temperature, by the same name and speak of them as representing different *forms* (or states of aggregation) of the same substance. It is only in the case of water and ice that we have two different words, and this is because of the great importance that the difference in properties has as regards our everyday life. In the eyes of the chemist, however, ice is only a particular form of the substance water, exactly as melted wax is one form of wax. The chemist, therefore, says: water is liquid above  $0^{\circ}$  and solid below this temperature.

The reason for giving the same name to these two apparently different substances lies in the fact that one is so readily changed into the other. It has never been found that any substance other than water is formed by the melting of ice, and similarly only ice, always having the same properties, is formed when water is cooled below the freezing or solidification point.

All that has just been said with regard to water holds equally well concerning all other substances that are known both in a solid and in a liquid state. The two forms correspond to a pair of like substances which undergo mutual transformations without giving rise thereby to a third substance.

Such transformations of a solid into a liquid, or the reverse process, may be regarded as *the simplest type of a chemical change*. Under certain conditions a substance disappears and a new one is formed in its place. Since it never happens that substances disappear without forming some other substance, or that a

substance is formed without the disappearance of one or more other substances, it is said that the original substance has been transformed into the new one. In such a sense as this, *chemistry is the study of the transformations of substances.*

As stated above, the solid and liquid states are ordinarily considered to be two different forms of one substance. For this reason such conversions are usually called *physical transformations.* We are here at the border line between physics and chemistry, and consequently such phenomena have to be studied carefully in both of these closely related sciences. From the point of view that water and ice are really two different substances, we are justified in considering the conversion process a chemical change.

**31. The conservation of weight.** — If we place some ice in a flask, make an accurate weighing, and afterwards weigh again when the ice has all melted into water, we shall find that *the liquid water weighs the same as the solid ice.* In passing from one form to the other there has been no change in weight. This experiment has been carried out with all possible precision, and not the slightest change has been found. Hence, when ice changes into water exactly the same weight of a new form appears as has disappeared of the old form.

This last statement holds not only for the melting of ice and all similar phenomena but *it holds equally true in every chemical transformation.* There are cases, to be sure, as in the burning of alcohol or petroleum, where a substance apparently disappears leaving nothing in its place; accurate investigations, however, have shown that this loss of weight is only apparent. When these liquids are burned, gases are formed which cannot be seen any more than air, or than the illuminating gas which streams out into the room if gas is turned on without lighting it at the burner. If the weight of all the substances present before combustion is determined, and then of all the substances present afterward, it will be found that the total weight is unchanged. Hence *the law of the conservation of weight.* If substances are present in a closed vessel and a chemical change is brought about, the total weight remains the same because the substances formed

weigh in the aggregate just the same as those that have disappeared.

**32. Natural laws.** — That these statements are in accordance with the facts has often been confirmed, although it is naturally impossible to test every new case that arises to see whether the law still holds. Yet everybody is convinced that the law likewise holds in every case which has not been studied. All our experience has shown that these simple and general relations are such that if we find a natural law to hold in many cases under conditions as different as possible, we are justified in assuming that it will hold for all other cases.

A natural law, therefore, is merely a concise, summarized statement of actually observed relations, in which it is reasonable to assume that the phenomena will be repeated in the future as they have been in the past. One must not think, however, that a natural law is a fixed rule in accordance with which nature *must* act whether she will or not. The law merely gives information as to how nature has acted previously. Inasmuch as we have found repeatedly that natural phenomena take place very regularly, we conclude in every case where such regularities have been found that they will be repeated in the future as in the past.

It is evident from this method of derivation that natural laws are subject to improvements which will make them more in accord with facts that are observed subsequently. These improvements usually arise from the discovery that the assumptions or conditions under which the behavior mentioned by the law takes place were not properly known or understood when the law was first formulated, so that it is necessary to define them somewhat differently. A certain part of the old law then holds, even though it may be modified in a given respect.

With regard to the law of the conservation of weight, this has recently been tested with all the precision possible with modern experimental skill, and it has been found that *the deviations from this law are not detectable*. At the same time, certain theories have been developed which suggest the possibility of there being such deviations, although it may be a very long time before it

is possible to detect them experimentally. Meanwhile we may confidently make use of the law, knowing that the error, if there is any, is less than it is possible for us to measure at the present time.

**33. Crystals.**—The solids that are formed when liquids freeze usually assume more or less regular shapes, called crystals. If the window pane is below  $0^{\circ}$  C. on a winter's day, moisture condenses upon it from the inside, forming a coating of solid ice which assumes the most varied shapes like stars, leaves, reeds, etc. These shapes are still more beautiful when ice forms out of doors on a very cold day as a light snow; often six-pointed stars of the most beautiful design are observed, and they are very regularly formed. Fig. 12 is made from photographs of such

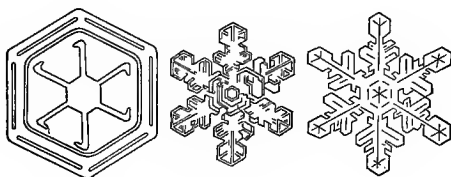


Fig. 12.

snow crystals. Even ordinary snow consists of similar shapes, although the crystals are as a rule broken and otherwise deformed so that it is harder to detect the regularities. In water that freezes on the street in half-dried puddles, it is often possible to find long crystals that are sometimes nearly a meter long.

Ice is by no means the only substance which exists in the form of crystals, but almost all liquids form crystals on being frozen. If, for example, some sulphur is melted in a large crucible, and then allowed to cool slowly until a crust forms on the surface, the whole interior will be filled with large yellow crystals, as will be seen if a hole is made in the surface of the sulphur and the liquid inside poured off. Similar experiments may be carried out with other fusible substances; particularly beautiful crystals are obtained with metallic bismuth, although too little of the metal should not be taken for the experiment.

**34. Laws of crystals.** — These crystalline shapes are to be regarded as properties which are peculiar to the various substances. Sulphur gives long prisms with slanting end-surfaces, bismuth gives right-angled steps, ice is always in the form of flat, six-pointed stars. If the crystalline form of a substance is known, therefore, the substance itself may be recognized thereby exactly as in the case of color and luster. There is, in fact, a special science of *crystallography*, which concerns itself with the study of these shapes and in which general laws have been discovered governing their growth. The most important thing is that all crystals are polyhedrons, *i.e.*, solids bounded by plane surfaces; crooked faces never occur. Moreover, it has been found that crystals of the same substance may indeed differ in shape and size, but *the plane surfaces which circumscribe the crystal always make the same angles with one another*. For this reason,

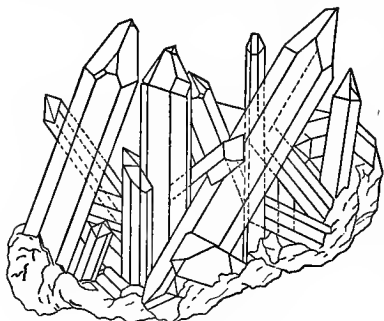


Fig. 13.

the different crystals of one and the same substance always bear a sort of family resemblance to one another, so that the substance is readily recognized to the practiced eye of the crystallographer or chemist. Fig. 13 represents a group of natural crystals of quartz. Although the different crystals in this group vary in size and shape, yet they are all made up of six-sided prisms, pointed at the free end by a six-sided pyramid. If the angles which the faces make with one another are measured, it will be found that the prisms are regular and the faces all inclined toward one another at an angle of  $120^\circ$ .

**35. Crystals and amorphous substances.** — Often the crystals of a substance are very small and imperfectly formed so that their shape cannot be recognized at the first glance. For example, marble is made up of tiny crystals, all intergrown, but which betray their nature by the peculiar glisten of the surface.



Since the boundary surfaces of crystals are always planes, a fractured surface of a piece of marble will consist of innumerable minute planes that are inclined toward one another at different angles and consequently reflect light in a peculiar manner: certain faces reflect the light directly into the eye and others do not; hence, if the piece of marble or the eye is moved, new faces mirror the light, so that glistening points appear here and there. By means of a magnifying glass it is possible to identify the separate crystal surfaces.

When, in such a way, the *crystalline nature* of a substance is known, it is possible to recognize even the imperfect crystallization, so that one can readily convince himself that the solid substances occurring in nature, as minerals, rocks, and ores, as well as all kinds of artificially prepared substances, appear again and again in the form of crystals, and that there are relatively few substances in which this property cannot be recognized. There exist, however, substances which do not crystallize, and which are called amorphous (shapeless). One of the best known of these amorphous bodies is glass. Although usually as clear and transparent as a pure crystal, it possesses no natural boundary faces, but is merely an immobile liquid which has the same shape that it possessed while in a mobile condition. If a crystal is hammered, it usually breaks so that new boundary surfaces are formed, called *cleavage surfaces*, which lie in the same direction as one of the faces of the original crystal. If, however, a piece of glass is broken by a blow from a hammer, rounded surfaces are formed and not planes. Glass is said to show *conchoidal* (like a shell) *fracture*, or cleavage. Most amorphous substances have a like property.

Amorphous solids have no definite melting point, this being a property of crystalline substances exclusively, and the crystalline nature may be recognized by means of it even when the crystal surfaces have been destroyed by polishing or in some other way. If, for example, a glass rod is held in a flame, it will be noticed that after some time the glass softens so that the rod may be bent. The hotter the glass, the softer it becomes, but there is no sharply defined melting point. With ice and other

crystalline substances it is quite different; at the temperature of the melting point the solid changes entirely into a liquid, and conversely, on cooling the liquid changes entirely into a solid at the same temperature, and the change in properties is not a gradual one.

Liquids are amorphous,<sup>1</sup> for they have no form of their own but assume that of the vessel containing them. Thus there are two ways in which a substance, on being cooled, may pass into the solid state. Either crystals which are solid and quite different from the liquid, are deposited at a definite temperature, or the liquid on cooling may gradually become more and more viscous until eventually it has some of the properties of a solid, namely as regards shape and elasticity. The latter solids are amorphous; during their formation there has never been a time when something quite different separated out from the liquid, but gradually the whole liquid has assumed the solid form without showing any indication of a definite melting point. Besides glass, pitch and resin are examples of amorphous substances.

**36. Temperature.** — When ice melts to water, by heating the mixture or by letting it remain in a warm place, the transformation of ice into water takes place at 0° C. This represents, in the first place, merely a definite *temperature*, which is recognized by the fact that the mercury in a thermometer is at a definite position. A thermometer, as every one knows, consists of a narrow, closed, glass tube with a bulb blown in the bottom; it contains more than enough mercury to fill the bulb. When the thermometer is heated, the glass becomes a little larger and at the same time the mercury expands, or occupies more space. The expansion of the mercury, however, is much greater than that of the glass; and, consequently, with rise of temperature the mercury rises in the glass tube. There is (within the limits of the thermometer) a definite place in the tube to which the mer-

<sup>1</sup>It is true that crystals exist in all degrees of hardness. Certain substances have recently been studied which are apparently liquids and yet show properties that are peculiar to crystals. These are called *liquid crystals*, and may be regarded as very soft crystals. They pass at a definite temperature into the true liquid condition and usually solidify at a definite lower temperature into true solids. (Translators.)

cury column will extend at a given temperature, and any particular position can be given a special name, just as a definite thing or a certain person is characterized by a word or name. There is not necessarily any similarity between the designated thing and the designation, and thus the names of the same thing may be altogether different in different languages. In the case of temperatures, there is the peculiarity that they all form a simple series, for all temperatures may be so regulated that a higher temperature always follows a lower one. Likewise the places on the thermometer where the mercury column stops at different temperatures are arranged so that there is a position on the thermometer corresponding to every definite temperature. In order to designate these positions properly so that they will be recognized, a graduated scale is placed on the side of every thermometer. Then there is a definite number which corresponds to each division on the scale, so that the thermometer registers a definite temperature when the mercury column is at a given height.

**37. The zero point.** — If a centigrade thermometer, which is the only one used in scientific work, is placed in a mixture of ice and water which is being well stirred, it will be found that the mercury column ends at the zero point. This is not at all remarkable, because in making thermometers the zero point is determined by marking the position of the mercury column when the thermometer is surrounded by a mixture of ice and water. The thermometer maker, however, did not use the same ice and water mixture that was used in the above experiment, but yet the mercury column was at the same place. This is evidence of the fact that we are making use of a natural law in determining the zero point of the thermometric scale. The law is: *when ice and water are present in contact with one another, the mixture of ice and water always has one and the same temperature.*

**38. The hundred point.** — It now remains to determine the length of the degree on the thermometric scale, and the ratio between the contents of the tube and its length varies greatly in different thermometers, so that equal distances on different instruments will represent quite different temperature intervals.

It is necessary, therefore, to determine another point on the scale, and for this the *boiling point of water is taken*. This behaves very much the same as the freezing point, *i.e.*, it is always at the same temperature, no matter where or how the boiling takes place.<sup>1</sup>

The thermometer is placed in boiling water and the point to which the mercury column rises is carefully determined. Then the distance between this and the freezing point is divided into one hundred parts. The melting point of ice is then designated as 0° and the boiling point of pure water as 100°. Temperatures below 0° or above 100° may be measured, but the length of the degree on the scale is kept the same.

In the Fahrenheit scale, the freezing point is marked 32° and the boiling point 212°, but this scale is less convenient, although still used for everyday purposes in English-speaking countries.

**39. Melting point and freezing point.** — The temperature at which ice melts, or fuses, is perfectly definite, and consequently this temperature, or the melting point, is a characteristic property of ice, or of the substance water in the solid condition, just as much as the density, color, etc. Even the bare statement that copper melts at a high temperature, and alcohol at a very low one, implies that these temperatures are definite for each individual substance. As a matter of fact this is perfectly general; *every pure substance is characterized by a definite melting point*, and since it can be determined with a very small fragment of the substance, this temperature is much used in practice for characterizing and recognizing substances.

How is it, then, with the reverse process, the solidification of a liquid? It is exactly the same. If instead of placing the mixture of ice and water in a warm room it is put out of doors on a cold winter's day, so that the ice no longer melts but on the contrary the water gradually freezes, we shall find that the

<sup>1</sup> To be sure, the atmospheric pressure must be taken into consideration, as it has an appreciable influence upon the boiling point. This influence, however, has been studied carefully, and it is very easy to apply the necessary correction. This will be explained more fully in the next chapter, in which boiling is discussed.

position of the mercury in the thermometer will remain unchanged, and hence *the mixture has the same temperature*. It is, therefore, immaterial in which way the transformation takes place, whether ice to water or water to ice, as long as both are present in contact with one another, the temperature remains unchanged.

Since we do not always have at our disposal a cold winter day in which to carry out such an experiment, we must find some way of getting along without it. This is possible by using a *freezing mixture*. If a mixture of ice and water is placed in a large vessel, the temperature of the mixture will be  $0^{\circ}$ . If we add a little common salt, or some alcohol, to the mixture, and stir it well, the temperature will fall still lower. Then if the beaker containing the mixture of ice and pure water is placed in this freezing mixture, the former is in colder surroundings exactly as if it were exposed to a winter atmosphere, and the water in the beaker gradually freezes. Nevertheless, the temperature will remain unchanged and the mercury will remain at the zero line.

If we call this point at which water changes into ice the freezing point, we can express what we have found to be true, in the statement, *the melting point and the freezing point are identical*. Both designate the temperature at which the liquid and solid forms of a substance can exist side by side. Whether one form or the other tends to increase in quantity makes no difference upon the temperature, as long as both forms are present.

Now what happens after all the ice has melted? Then, if the surrounding temperature is higher, the temperature of the water gradually rises. Or, conversely, if the water is in a cold place, after it has all been frozen into ice, the temperature of the ice will fall until it reaches that of the surroundings. Either of the homogeneous substances, water and ice, may exist at different temperatures, ice at any temperature below zero and water at temperatures above zero.<sup>1</sup> But zero is the boundary line which limits the temperature fields of ice and of water.

<sup>1</sup> This last statement will be modified somewhat in the following discussion.

Other substances behave like water and ice in this respect, except that the melting points, or the temperature limits between the solid and liquid, lie at different points on the thermometric scale.

**40. Supercooling.**—When two things which would otherwise influence each other can exist side by side indefinitely without change, they are said to be in *equilibrium*. Originally this word was used to designate the state which is reached, as we have seen, when the weights in the two pans of a balance are equal; later the word has been used in a more general sense. Thus we may say that *water and ice are in equilibrium at 0°*.

In order to establish an equilibrium, it is necessary that each of the things in equilibrium shall be present. Thus in the case of a balance, equilibrium is disturbed if a weight is taken away. In exactly the same way, there is no equilibrium between water and ice unless both forms are present at the same time. Thus if the surrounding temperature is above or below 0° either the ice or water gradually disappears and then there is no longer a state of equilibrium between the two. There is another interesting

case in which the second form is kept absent. If water is present in a closed tube, which may conveniently be of the shape shown in Fig. 14, and the tube is placed in a freezing mixture which is at about  $-5^{\circ}$ , the water will not freeze no matter how long it is kept at this temperature. It will not freeze even if the contents of the tube are shaken. If the freezing mixture is made colder by the addition of more salt, until the temperature is  $-10^{\circ}$ , still the water will not freeze unless it is violently shaken. If all jar is carefully avoided, the water may even be cooled to  $-25^{\circ}$  without the appearance of any ice; it is then formed immediately on shaking. In each case all the water does not freeze at once, but a few ice crystals float in the remaining liquid.



Fig. 14.

The lower the temperature the larger the amount of ice that first forms. When the ice begins to form, the temperature of the water at once rises to  $0^{\circ}$ , as can be shown if the experiment is carried out in a stoppered bottle with a

thermometer dipping into the water (Fig. 15). This phenomenon, which can take place with any substance if cooled in the liquid state below its freezing point out of contact with the solid, is called *supercooling*. The experiments prove that a slight supercooling can be prevented only by contact with the solid form (ice) but that a greater degree of supercooling can be prevented by shaking. If a piece of solid glass rod is introduced into the tube (Fig. 14) before it is sealed, ice will appear, on shaking, at a higher temperature than if water alone were present.

The explanation of supercooling is based on the fact that a state of equilibrium between water and ice at  $0^{\circ}$  requires the presence of both forms. If, by carefully sealing the vessel, the accidental introduction of traces of ice is prevented, it is not necessary that ice should form and the water remains liquid. Water under these conditions is, to be sure, not a perfectly stable form, because it would go over into ice were the latter present. The lower the temperature goes, the less stable liquid water becomes, until finally the shock brought about by shaking is sufficient to cause the formation of the first trace of ice. The amount of ice then increases until equilibrium between the solid and the liquid forms is reached. Since this can take place only at  $0^{\circ}$ , this temperature is at once assumed by the mixture.

**41. Heat of fusion and of solidification.** — Why does not water at once freeze after it has been cooled below  $0^{\circ}$ , and why is only a part of the water that has been supercooled converted into ice? We have seen that a fixed temperature corresponds to the solidification point of water and of all other liquids, and we should, therefore, naturally expect that the slightest lowering of the temperature below  $0^{\circ}$  would at once cause complete solidification of the water, whereas we have found by experiment that water may be cooled below  $0^{\circ}$  and kept at this temperature for a long time before it all freezes. Similarly, it is well known

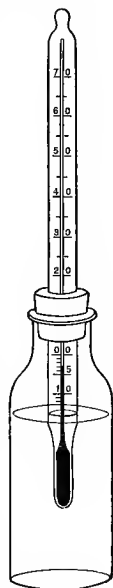


Fig. 15.

that a cake of ice does not all melt at once when placed in a warm room; it remains for a long time at the temperature of  $0^{\circ}$  and is gradually transformed into water.

The cause is the same in both cases. In order to convert water into ice, a large amount of heat must be withdrawn from the water at  $0^{\circ}$ , and only in proportion as this heat is withdrawn is it transformed into ice. Conversely, a large amount of heat must be taken up by ice at  $0^{\circ}$  in order to convert it into water at the same temperature, and only in proportion as this heat is taken up by the ice will it melt.

Weigh a piece of ice of about 10 g. upon a piece of filter paper, which absorbs any water that is on the surface of the ice, and then weigh the paper by itself in order to obtain by difference the exact weight of the ice itself. Place the ice in a beaker containing a known weight of water (200 to 500 g.), the temperature of which is accurately measured by a thermometer graduated in tenths of a degree. Stir with the thermometer until all the ice has melted. The temperature of the water will become much lower on account of the fact that heat was taken from it in melting the ice.

To determine the amount of this heat, it is necessary to know that the *unit of heat* commonly used in scientific work is called the *calorie* and is *the quantity of heat necessary to raise the temperature of 1 g. of water  $1^{\circ}$  C.* If now  $e$  represents the weight of the ice and  $x$  the unknown quantity of heat which is required to melt 1 g. of ice into water at  $0^{\circ}$ , then  $ex$  heat units, or calories, will be required to convert  $e$  grams of ice at  $0^{\circ}$  into water at the same temperature. Let the temperature of the water be  $t_2^{\circ}$  after the ice has all melted, and let  $t_1^{\circ}$  represent the original temperature. Then  $et_2$  calories are required to heat the melted ice from  $0$  to  $t_2^{\circ}$ . All this heat comes from the water originally present. If the weight of this water is  $w$ , then the quantity of heat which was given up as its temperature fell from  $t_1^{\circ}$  to  $t_2^{\circ}$  is  $w(t_1 - t_2)$  calories. It is evident, then, that  $ex + et_2 = w(t_1 - t_2)$ , and from this equation the value of  $x$  may be computed. In carrying out the experiment in the above manner, a certain amount of heat is supplied by the surroundings, so that the value



of  $x$  as found will always be somewhat less than 80 calories, which is the true value.

All other substances behave similarly. Every time a solid is converted into a liquid, there disappears a certain amount of heat, which is proportional to the weight of substance present and depends upon its nature. The quantity of heat required to melt 1 g. of the substance is called the *specific heat of fusion*.

One is justified, therefore, in regarding the transformation from the solid into the liquid state as a combination of the substance with a certain amount of heat, for exactly the same quantity of heat is set free if the liquid substance is again changed back into the solid form.

The fact that heat is set free by the solidification of a liquid is more apparent in the case of a substance having a somewhat higher freezing point than that of water. Take, for example, some of the salt which is used in photography as "hypo" and which bears the chemical name *sodium thiosulphate*, place it in a small flask and melt it over a flame. When all the salt is melted, remove the flask from the flame and place a wad of cotton in its neck. It is then possible to cool the liquid to room temperature without the formation of any solid. If, however, a small piece of the same salt is dropped into the cold solution, the liquid at once begins to solidify in the form of beautiful crystals, and the resulting heat of solidification causes the temperature to rise to  $56^{\circ}$ , which is the melting point of the salt.

**42. Equality of the heat of fusion and the heat of solidification.** — The fact that exactly the same quantity of heat is set free when water freezes as must be supplied to melt the same weight of ice, can be shown by a direct experiment. Moreover, this principle may be deduced in general for all substances that are known in both the solid and liquid states on the basis of the general empirical principle that *heat in unlimited quantities and without other change cannot be formed or made to disappear*. This last theorem is a particular case of the general law of *conservation of energy*, or the *impossibility of perpetual motion*. It is the most general law of modern science and we shall constantly meet with it in different forms.

If the heat of fusion of a given quantity of ice were less than the heat of solidification of the same weight of water, then less heat would be required in melting than is set free on solidifying, and hence a certain quantity of heat would remain if a definite weight of ice were first allowed to melt and then were transformed back into ice again. By repeating the process over and over again the amount of residual heat could be multiplied indefinitely, or, in other words, heat would be created out of nothing. This, according to the sum total of all our experience, is impossible.

If, on the other hand, the heat of fusion were greater than the heat of solidification, it would be possible to destroy any desired amount of heat without eventually changing the world in any respect; this is again contrary to all our experience. It is, therefore, a necessary consequence that the two quantities of heat should be equal.

Inasmuch as the same sort of reasoning may be applied to all imaginable transformations in which a substance is transformed from a condition A to another condition B, and then B is transformed back into A, it follows that in every case the quantity of heat which is evolved or expended in transforming A into B is equal to the quantity of heat expended or evolved in the reverse transformation of B into A. We shall subsequently make use of this principle repeatedly.

**43. The conservation of energy.** — Formerly the heat of fusion of solid substances was called their *latent* or hidden heat, inasmuch as it was assumed that this heat that disappears was present in some unrecognizable form since “the same,” *i.e.* an equal, quantity of heat is evolved when the substance freezes again. At present the change of condition of the substance is regarded as equivalent to the quantity of heat that has disappeared, or rather the new condition represents the transformation product of the original substance with this quantity of heat. In other words, this heat is no longer supposed to exist in the form of heat, because it has been transformed into something else. This is apparent in the new nature of the substance (liquid instead of solid). In the same way that it is necessary to perform

work in transforming a tree into logs suitable for fuel, or in reducing a large piece of a solid into a powder, so it is necessary to perform work in order to convert a solid into a liquid. In this case work is performed by the heat that is expended, just as the steam engine converts heat into work. By friction it is possible to obtain heat again from the work done, and in fact the same amount of heat can be obtained as was expended in the performance of the work. Work and heat, therefore, are two different things which can be transformed into one another. The nature of the work that is performed in transforming a solid into a liquid is called *chemical work*, because this transformation really represents a chemical change.

The general name *energy* is given to all the different things which can be converted into work and which result from work. Heat is, therefore, a form of energy. All kinds of energy can be transformed into one another and in every case an equivalent quantity of some form of energy appears when another form disappears. This is a very general empirical law and is based upon the fact that it is not possible in any way to create perpetual motion, *i.e.*, a machine which will create work out of nothing. For if from energy A more of energy B is formed than is necessary to produce the original amount of A by the reverse transformation, then the excess of B could be retained, and by repeating the transformation backward and forward, any desired amount of B could be created from nothing, and be transformed into work; thus work (which can always be accomplished by energy) would be created out of nothing and perpetual motion would be possible.

**44. Cooling with ice.** — The property which ice has of requiring a large amount of heat in its melting, without there being any change in its temperature, is utilized for purposes of refrigeration. Before one gram of ice is melted, a quantity of heat must be supplied which would be sufficient to raise the temperature of 1 g. of water from 0° to 80° C. Since many substances such as meat, fish, fruit, etc., which undergo change quite readily, will keep much better in the vicinity of 0° than at a higher temperature, ice is used for refrigeration in cellars, ice chests, transporta-

tion vessels, cars, etc. Many modern explosives and gun-powder are readily decomposed in warm places, so that ice is used to cool the grinding rooms as a safety precaution.

**45. Separation by fusion.** — The difference in melting points may be used as a basis for effecting a separation in a mixture of solid substances. We know that solid substances in the form of a fine powder do not separate of their own accord after they are well mixed, although gravity suffices to effect a separation if one constituent of a binary mixture is a solid or a liquid. If, then, a mixture of two solid substances is heated until one of them is liquefied, a separation will take place of itself by the action of gravity.

This process is used, for example, in separating the metal bismuth from its gangue minerals; the ores are placed in inclined tubes and heated, whereupon the metal melts and flows out at the bottom, leaving the solid impurities behind.

Similarly sulphur is separated from clay in Sicily. The lumps of sulphur and clay, as they occur in nature, are piled up in heaps, like charcoal piles, which are built upon an inclined piece of ground, and the sulphur is lighted at the bottom. The heat suffices to melt the sulphur in the pile, and the liquid runs off into a pit at the bottom, leaving the clay behind.

#### § 7. BOILING AND LIQUEFYING.

**46. Evaporation.** — No matter how much a solid substance is cooled, it always remains a solid, and there is no case known of a substance becoming a liquid or a gas as a result of being cooled. If, however, a liquid is heated it does not retain its liquid state indefinitely, but at a definite temperature it is converted into a gas. Gases that are obtained by the heating of liquids are called *vapors*, although this is in reality a superfluous name, as it does not indicate any particular properties. In reality all gaseous substances are formed at definite temperatures from liquids, and conversely all gases can be converted into liquids by cooling them sufficiently.

As in the case of the transformations of solids into liquids, the temperatures at which the various liquids are converted into

gases are distributed throughout the whole range of known temperatures. The temperature at which a liquid is converted into its gas (or vapor) is called the *boiling point* of the liquid. These boiling points, like the melting points of solids, are dependent upon the nature of substances, and serve similarly for their characterization and identification.

**47. Boiling.** — If water that has been freed from air by a previous boiling is heated over a flame in a glass flask, with a thermometer inserted, the temperature of the water will rise higher and higher until finally the mercury approaches the 100° mark. Then, at the bottom of the flask, where the water is hottest, bubbles of gas begin to form, detach themselves, and rise in the liquid. At first they do not get far but disappear before the surface of the liquid is reached. At the same time a peculiar noise is made in the flask which announces the beginning of boiling.

The bubbles now rise higher and higher and soon begin to reach the surface of the liquid, where they burst. A cloudiness then appears in the neck of the flask, and on inserting a cork, the steam exerts a pressure against it, seeks to throw it outward, and escapes with a hissing noise between the crevices in the cork.

At this point the transformation of the liquid water into gaseous water is in full progress. The upper part of the flask appears perfectly clear and transparent, a proof of the fact that water vapor is itself colorless and transparent. The white so-called "clouds of steam" which are thrown off, especially in winter, when a locomotive is in operation, do not consist of water vapor but of liquid water. The water is condensed from the vapor by the cooling that it experiences from the surrounding air, and since this cooling process takes place very quickly, the water is in the form of innumerable tiny drops. If subsequently the white cloud dissipates in the air or disappears from view, something that happens more quickly in summer than in winter, it is because the liquid drops have been transformed again into vapor which dissolves in the atmosphere and becomes invisible, for a colorless gas cannot be seen even when mixed with another gas (p. 29).

Just as water can be transformed into a gas by simply heating it, so can all other liquids. Alcohol boils at  $78^{\circ}$ , petroleum oil much higher than water. Thus every individual substance has its characteristic boiling point.

Mercury boils at a temperature of  $356^{\circ}$ , which is not very high, and as we are not accustomed to think that a metal can be boiled it is well to carry out the experiment. Heat a little mercury in a test tube, or in a small round-bottomed flask, and notice that there soon forms on the upper, colder portions of the glass a deposit consisting of tiny gray drops which, when examined under a magnifying glass, will be seen to have the luster of mercury. Eventually the mercury will begin to boil vigorously, and one sees that the vapors are colorless and transparent, like most other vapors. Since the boiling point is relatively high, the greater part of the vapors will condense within the tube or flask. The vapors of mercury are poisonous, so that the experiment should be carried out under the laboratory hood to prevent any of the vapor being inhaled accidentally. Mercury poisoning causes a flow of saliva.

As it is possible to recognize very small amounts of mercury when condensed as a gray deposit in the upper parts of a heated vessel, frequently the presence of the metal in a mixture is detected in this way.

**48. Liquefaction.** — Conversely, all substances met with under ordinary conditions in the form of gases can be converted into the liquid state by cooling sufficiently.

For a long time there were certain gases, *e.g.* the air, which could not be liquefied because it was not known how to lower the temperature sufficiently. Quite recently this has been accomplished, however, so that to-day even liquid air has become a commercial article. It is kept in vessels (Fig. 16) which are provided with a double glass mantle, the space between the glass

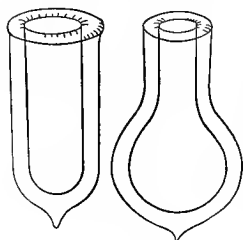


Fig. 16.

walls being carefully pumped free from air. By means of such protection the conduction of heat through the walls is diminished

to a remarkable extent,<sup>1</sup> so that the liquid air, which must remain very cold as long as it is in the liquid state, can be kept in them for days. If liquid air were placed in an ordinary vessel, it would soon begin to boil and be transformed into ordinary gaseous air.

**49. Variability of the boiling point.** — The boiling point of a pure substance behaves exactly like the melting point and represents a perfectly definite temperature which will always be the same with the same substance under the same conditions. It is suitable, therefore, for determining a second point on the thermometric scale. Water is used in practice for the determination of these two points, as it is the substance easiest to procure in a pure condition.

If, however, experiments are carried out carefully with a sensitive thermometer, it will be found that the boiling point is not exactly the same on different days. This depends upon the atmospheric pressure, shown by the barometer reading. The higher the barometric pressure, the higher the temperature at which water boils, and conversely. The boiling point of water, therefore, and of all other substances, is dependent upon the atmospheric pressure. If the barometer reading is exactly 76 cm. then the temperature at which water boils is exactly 100°. For every centimeter difference in barometer reading there is a corresponding change of 0.37° in the boiling point. If a thermometer is graduated at a time when the atmospheric pressure is not equal to that of 76 cm. of mercury, the 100° mark is not made at the temperature of boiling water, but its position is computed in accordance with this known effect that the difference in atmospheric pressure has upon the boiling point.

**50. Pressure.** — The pressure exerted by the ocean of air in which we live is measured by an instrument called a *barometer*. The simplest form of barometer consists of a glass tube, closed at one end, filled with mercury and then inverted over a dish of mercury. Another form of barometer is bent at the bottom, so

<sup>1</sup> Such bottles are now being used more and more in everyday life. If the liquid is hot as it is poured in, it will keep so for a very long time; or if it is cold, it will stay cold.

that the mercury rises in a second arm which is left open; the principle is the same in each case. If the tube is about 80 cm. or more in length, an empty space will be found in the closed tube above the mercury column, and the mercury sinks until it is about 76 cm. above the level in the open vessel or in the open tube. This height is a measure of the atmospheric pressure. Another form of barometer, and one we shall use later on for other purposes, is obtained by connecting two tubes by rubber

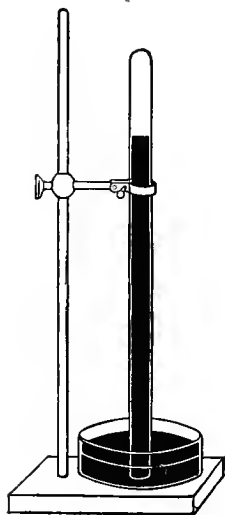


Fig. 17.



Fig. 18.



Fig. 19.

tubing and then filling with mercury (Fig. 18). One of the tubes is provided at the top with a stop-cock, and before closing the latter the tube is entirely filled with mercury; the other tube is left open. Because of the flexibility of the rubber tubing, the two tubes may be moved up and down with reference to one another; if the open one is lowered until the difference between the heights of the mercury columns is more than the 76 cm., the level



of the mercury in the closed tube will fall until the difference between the two mercury levels corresponds to the atmospheric pressure.

A pressure of exactly 76 cm. of mercury is called an *atmosphere*. It is commonly used as a unit in measuring pressures.

According to the laws of hydrostatics, the pressure exerted by a column of liquid is proportional to its height and to its density. Since mercury is 13.6 times as dense as water, it follows that a column of water exerting the same pressure would be 13.6 times as high as one of mercury. In other words, a barometer in which water was used instead of mercury would have to be  $76 \times 13.6 = 1034$  cm. long, somewhat over 10 meters.

Pressure may also be measured in terms of the weight exerted upon a definite surface. The unit of surface is the square centimeter; a water column 1033 cm. high and of 1 sq. cm. cross section contains 1033 g. of water, or a little more than one kilogram. For technical purposes, pressures are often expressed in kilograms per square centimeter and the pressure of an atmosphere is considered equal in round numbers to 1 kg. per sq. cm.<sup>1</sup> For scientific purposes, however, the atmosphere is defined as above.

**51. Vapor pressure.** — A liquid boils when the pressure of its vapor has become great enough to overcome that of the atmosphere, *i.e.*, when its vapor pressure has become just a little more than that of the atmosphere. If, therefore, the boiling point varies with the pressure, this must be due to the fact that *the vapor pressure changes with the temperature*. This important and general fact can be observed and measured by the following experiment.

The communicating tubes shown in Fig. 18, which contain mercury and are connected with one another by means of rubber tubing, are used for the experiment. In the closed tube is placed a little of some volatile liquid, such as ether or benzene. Water could be used, but as its boiling point is higher it is not so convenient, and the change in vapor pressure with the temperature takes place with all vapors.

<sup>1</sup> This is equivalent to 14.2 lbs. per sq. in. In the English system, however, an atmosphere is taken as 14.7 lbs. per sq. in.

In order to be able to change the temperature at will, the closed tube is surrounded by a glass mantle, into which either hot or cold water may be poured. At first the water in the mantle has the room temperature.

If now the movable tube is lowered, the mercury column in the other tube will fall and the liquid begin to boil. If there were no liquid in the tube, the mercury column would not fall until the level of the mercury in the open tube was 76 cm. (which we shall assume to be the barometer reading), lower than the top of the mercury column in the closed tube. If we measure the difference in level, we shall find that it is a smaller number,  $m$ . This value subtracted from the barometric reading gives the vapor pressure of the liquid,  $76 - m$ .

If we raise and lower the movable tube, and measure each time the difference in height between the two mercury columns, we shall always find at any given temperature the same value of  $m$ . It follows, then, that *the vapor pressure of a liquid is the same, irrespective of the amount of liquid that has evaporated. The vapor pressure, therefore, is not dependent upon the amount of liquid or vapor present, but depends solely upon the temperature and the nature of the liquid.* This is an important natural law. It is similar to the law that we have found to govern the coexistence of water and ice, or of the solid and liquid forms of any substance.

In reality, this law could be deduced from the fact that water boils at  $100^\circ$  irrespective of the amount of water taken, the amount of vapor present or the size of the vessel containing it. Since none of these factors, then, influences the boiling point, it follows that they have no effect upon the relation of the liquid to its vapor.

It is evident from this simple example that everyday phenomena if studied closely may lead to important conclusions. A celebrated example of this is the story that Newton discovered the law of gravitation from watching the fall of an apple. It requires, to be sure, an unusual mind to draw such conclusions from common, everyday experiences, but the possibility of important discoveries being made in this way nevertheless remains.

It is certainly desirable, after drawing such a conclusion, to test it by carrying out many experiments in which the conditions are varied as much as possible, for one can never be sure that some essential feature has not been overlooked. For this reason experiments such as that just described and the following are well worth performing.

**52. Vapor pressure and temperature.** — If now a little ice is placed in the water mantle, the vapor pressure will be found to diminish, and *for every temperature a definite pressure can be found at which vapor and liquid exist side by side.* If the attempt is made to increase the pressure by raising the movable tube, then some of the vapor is condensed so that the former pressure is again established, until, finally, all the vapor has been converted into liquid, and then the pressure can be raised as much as desired. Similarly, by lowering the tube, and thus increasing the space above the mercury column, eventually all the liquid can be converted into vapor, but it will not be possible to diminish the pressure in the upper part of the closed tube until all the liquid has been vaporized, for the vapor, like any gas, expands in inverse proportion to the pressure applied to it.

By introducing hot water into the mantle the pressure of the vapor increases and it becomes necessary to raise the movable tube. When the columns of mercury in the two tubes are of equal length, the pressure is equal to an atmosphere, and the temperature of the water mantle shows the boiling point of the liquid under atmospheric pressure. If the water is made still hotter, the outer pressure must be made greater by raising the movable tube above the other.

In such a way as this it is possible to obtain two series of corresponding values — temperatures on the one hand and pressures on the other. For every temperature there is a certain pressure, and corresponding to every definite pressure there is one temperature and only *one*. This may be expressed as follows: *vapor pressure and temperature are functions of each other; the vapor pressure is a function of the temperature just as much as the temperature is a function of the vapor pressure. Each is an explicit function of the other.*

The mutual relation can be pictured if we imagine the thermometer scale placed in a horizontal position and over each degree on the scale a perpendicular erected of the same height in centimeters as the mercury column that shows the corresponding vapor pressure ( $76 - m$ ). As these lengths would be too great to put in a book, it is best to use for these vertical distances a fraction of their true value, just as a geographical map is drawn to scale. Then, if the true dimensions are stated on the margin, there is no need of knowing the exact size of the drawing. Thus in the plot shown in Fig. 20 each of the smallest divisions in a horizontal direction (abscissas) represents  $1^\circ$  of temperature, and each division in a vertical direction (ordinates) represents 1 cm. of a mercury column, although in the drawing these distances are less than 1 mm.

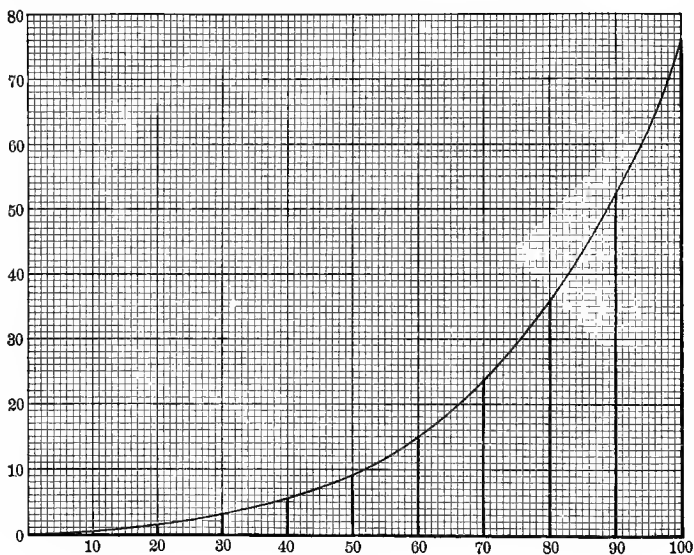


Fig. 20.

In Fig. 20 it is assumed that a measurement is made at every  $10^\circ$  temperature interval and the vertical black lines represent the heights of mercury columns corresponding to the vapor pres-

sure at these temperatures. If the upper points of these lines are joined by a line, a regular curve is obtained. The corresponding values are given in the following table.

VAPOR PRESSURE OF WATER.

0°	0.46 cm.	60°	14.92 cm.
10°	0.92 cm.	70°	23.38 cm.
20°	1.74 cm.	80°	35.55 cm.
30°	3.16 cm.	90°	52.60 cm.
40°	5.50 cm.	100°	76.00 cm.
50°	9.22 cm.		

If we wish to know what the vapor pressure is at say 85° or at 57°, any one would assume that the desired value will lie between the measured pressures at 80° and 90°, or between 50° and 60° in the second case. If the experiment is carried out, this assumption will prove correct. This leads to the thought that perhaps all vapor pressures corresponding to intermediate temperatures can be read from the curve shown in Fig. 20, which connects the observed pressures.

**53. The law of continuity.** — The expectation is in fact fulfilled. It is an expression of the general law which reads: *Most natural phenomena take place continuously over a considerable field.* In other words, if one value, *e.g.* the temperature, varies slightly, then the other value, the pressure, varies a correspondingly small amount, and every value falls regularly between the neighboring ones.

This general law is often expressed by the statement: "Nature makes no jumps." This is only true in a certain sense. The transformation of water into ice may be regarded as a jump, for there is a sudden change in properties when water is converted into ice, and the same is true when water is transformed into vapor. Every property, with the exception of the weight, changes suddenly in such a case, and in this sense nature certainly makes a considerable jump. On the other hand, it is not true that some of the properties change continuously while others change suddenly. If the temperature is changing continuously, the same is true of the vapor pressure, the vapor

density, and almost all the other properties. Some of them change much faster than others, but they all change continuously.

**54. Graphic representation.** — On the basis of the law of continuity it is possible to acquire knowledge of values that have not been studied. If, as described above, a continuous line is drawn connecting the upper ends of the perpendiculars shown in Fig. 20, the points on this line will give the vapor pressures for all those intermediate temperatures at which no measurements were made, and if tested by experiment, it will be found that such values are correct. This process of determining intermediate values is called *interpolation*, and in this particular case it is *graphic interpolation*. The relation between the measured values of pressure and temperature may be expressed by an algebraic formula so that one value may be computed if the other is given. Such a formula, also, may be used for the determination of intermediate values, and in this case it is *mathematical interpolation*. The graphic interpolation is usually much simpler, and if care is taken the values obtained are sufficiently accurate. Graphic representation, as shown above, has moreover the advantage that it gives a comprehensive summary of the entire phenomenon, and for this reason it is much used in the study of natural science.

From Fig. 20 one sees not only that the vapor pressure increases with rise of temperature but also that the increase is greater with every degree rise in temperature. This is shown by the fact that the line constantly becomes steeper and hence the increase in pressure for two equal temperature intervals is greater as the temperature rises.

This is the general nature of all vapor-pressure curves. In every case the pressure increases with rise of temperature, and the increase per degree of temperature constantly becomes greater. All these curves, therefore, are arched toward the base line, or convex. The curves vary, however, with different liquids, corresponding to the different boiling points.

**55. Boiling by cooling.** — The same relations may be shown by the following striking experiment. Water is heated to boiling

in a round-bottomed flask until it boils vigorously. The flask is then closed with a tightly fitting cork and, at the same time, removed from the source of heat. If now the flask is inverted and cold water poured upon it, boiling will again take place, although the contents of the flask must be constantly growing colder. The phenomena may be repeated several times, and yet each addition of cold water serves to cool the contents of the flask.

In order to understand this experiment it is well to repeat it in a somewhat different manner (Fig. 21). This time the flask is provided with a means of measuring the pressure, *i.e.*, with a *manometer* to show exactly what is taking place within the flask. The manometer consists here of a tube bent twice at right angles, having the longer arm as long as a barometer tube (about 80 cm.) and dipping into a vessel with mercury; the shorter arm enters the flask through a tightly fitting stopper.

The water in the flask is heated to boiling and bubbles escape through the mercury seal. These bubbles are at first only the air that is being expelled from the flask and the tube by means of water vapor. When the water vapor is free from air, the bubbles will condense as they come in contact with the cold mercury and there will be a metallic hammering caused by this condensation.

If now the flame is removed, the flask and its contents at once begin to cool and the mercury rises slowly in the tube. This is evidence of the fact that the pressure within the flask is becoming less and less, for at all times it amounts to the atmospheric pressure less the pressure corresponding to the mercury column in the manometer tube. The colder the water in the flask, therefore, the smaller becomes the pressure of the water vapor.

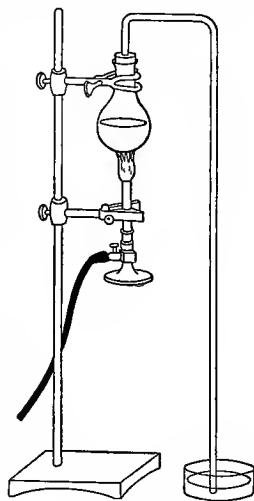


Fig. 21.

Moreover, if cold water is poured over the flask, the mercury rises suddenly in the tube, and the water in the flask, which is constantly becoming colder, begins to boil again, whereby the mercury column drops a little, but never to the point where it was before the cold water was added.

This is easily explained. When the cold water is poured upon the flask, the water vapor near the walls is at once condensed to liquid, causing the pressure within the flask to fall suddenly. In fact the pressure of the vapor in the flask becomes so small that the water is hot enough to boil and vapor is produced to make the pressure within the flask correspond to the vapor pressure of water at the temperature prevailing. Every time the cold water is poured upon the flask the mercury in the tube rushes upward, the water boils a little, and the mercury then sinks again, but not to its former position, for the temperature of the water is constantly falling and its vapor pressure is, therefore, becoming smaller.

It will also be noticed that the bubbles of vapor do not form at the bottom of the flask, as is customary, but at the surface.

**56. Distillation.** — If water vapor is cooled below  $100^{\circ}$  it again becomes liquid water. The process of boiling a liquid and then condensing the vapor is called *distillation*, and for this purpose various forms of *distilling apparatus* are in common use.

In the chemical laboratory, retorts and flasks with condensers are often employed. A retort is a flask with a long neck bent downwards. The liquid is placed in the retort, which,

for the sake of convenience, is often provided with a special opening (*tubulus*) for filling and for introducing a thermometer. The liquid in the retort is heated to boiling, and the vapors lead into a flask which is placed over the neck of the retort (Fig. 22).

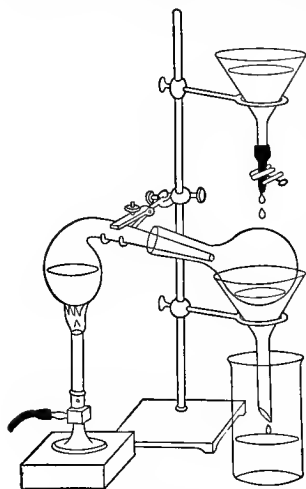


Fig. 22.



After the distillation has begun, steam is soon visible in the flask, called the *receiver*, and condenses upon the walls in small drops. The drops run together and the distilled water (*distillate*) collects in the bottom of the receiver. Before very long the receiver itself becomes so hot that it does not condense the steam, which now escapes. This heating of the receiver is due partly to the temperature of the steam, but more especially to the large quantity of heat set free when steam condenses into water and which is equivalent to the heat required to convert water at  $100^{\circ}$  into steam of the same temperature.

If, therefore, it is desired to continue the distillation, some means must be provided to take away the heat that enters the receiver with the steam. To this end cold water from a funnel above (Fig. 22) is allowed to trickle over the receiver, which is itself supported at a suitable height by means of a second funnel, and the warmed water runs off into a beaker placed beneath. Now the steam no longer escapes from the receiver, and the distillation may be continued as long as any liquid remains in the retort.

**57. Counter currents.** — Another and more convenient apparatus for distilling is shown in Fig. 23. Instead of a retort a *distilling flask* is used. The side arm of the latter is connected with a condenser in which the liquefaction, or condensation, of the vapors takes place. The condenser consists of two tubes, one within the other, and in the space between them a current of water is caused to flow. The vapors are passed through the inner tube and cooled by the water flowing on the outside. As the condenser water soon becomes hot, and since the aim is to cause the hot vapors to flow out in the form of a cooled liquid, the cold water is allowed to enter at the bottom and flow out at the top of the condenser, so that the water as it flows constantly becomes hotter, and the vapor, passing in the reverse direction through the inner tube, meets the hot condenser water first and the cold last. Both streams, therefore, move in opposite directions, so that a condenser is a practical application of the principle of *counter currents*, which plays an important part in chemical technique. In this way the greatest economy is

obtained, whether with regard to the amount of heat utilized or of material employed.

If we examine the condenser critically, after it is once in operation, we shall find that it is hottest at the upper part, for it is here that the vapors enter. This is the place where the water, which is already quite hot, exerts its last cooling effect, and since the fresh, hot vapors are the easiest to cool, they are partly condensed here. The condenser water, therefore, may leave the condenser in an almost boiling condition after it has effected all possible

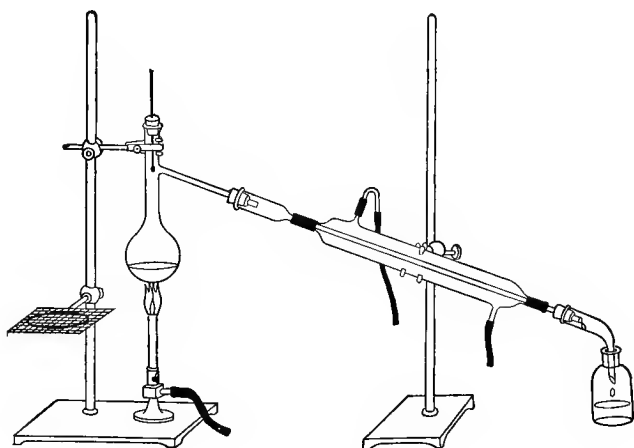


Fig. 23.

cooling of the vapor. The temperature of the water in the condenser gradually becomes colder toward the bottom. At the place, where the cold water enters, the last traces of vapor are condensed, so that none escapes, and for this purpose the cold water is required, because warm water effects only a partial condensation.

If, on the other hand, the condenser were set up so that the cold water entered at the top and flowed out at the bottom, it is true that the greater part of the vapors would be condensed, but the last traces would probably remain as vapor, for the simple

reason that the water would be too hot at the bottom. In that case the only way to effect a complete condensation would be to use a great deal more water in the condenser.

By means of the counter current the parts which mutually affect one another are made as little different as possible. In the case of the vapor the temperature becomes colder and colder as the bottom of the condenser is approached, and the temperature of the condenser water varies likewise. The hottest vapor comes in contact with the hottest water and the coldest vapor with the coldest water, so that in all parts of the condenser the

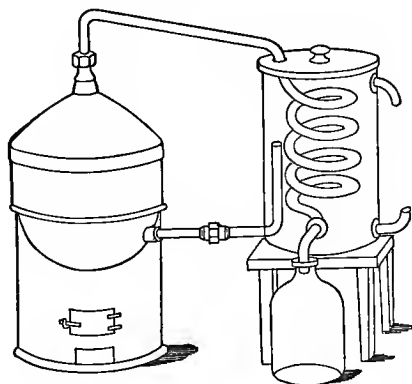


Fig. 24.

work is carried out with the least possible temperature fall. The reverse arrangement would necessitate a great temperature fall at the place where the vapors and water enter, and would necessitate a great waste of water. The principle of counter currents, therefore, affords in every respect the best and most efficient condensation.

This very simple but equally important principle will be repeatedly encountered under other conditions. It forms the basis of economical technique, and not alone in chemistry.

We find that the same principle is applied in apparatus designed for the distillation of large quantities of water (Fig. 24). In this case, however, the inner tube takes the form of a coil or

worm, simply to economize in space, and the whole is placed in a large tank of water. Even in this case, however, care is taken that the water enters below and the vapor at the top, so that the hottest vapor comes in contact with the hottest water, and conversely.

**58. Distilled water.** — The question naturally arises, Why is water distilled? It has already been shown that vaporization and liquefaction are perfectly reversible processes, so that distilled water is nothing but pure water. And when it is recalled that even our natural water was first in the air as vapor before it was condensed to rain or snow, in which form it fell to earth and went to make up the springs, brooks, and rivers, one might with perfect right say that all water is distilled water, in fact that it is water which has been distilled over and over again.

Now all this is perfectly true, and it would not be at all necessary to distill again in the relatively small apparatus devised by man, were it not for the fact that nature's distilling apparatus is faulty with regard to the receiving or collecting apparatus. The stones and earth with which the rain water comes in contact are not composed of perfectly insoluble substances. Accordingly, the water soon takes up from its surroundings various solid and gaseous substances, so that the water of all our springs, rivers, and lakes is no longer to be regarded as pure but as a solution containing many substances taken from the earth with which it comes in contact.

The fact that spring water, for example, is not pure water is recognized by the fact that it gives rise to the formation of a *boiler scale* which settles out in the vessels that are used to boil and evaporate water. If a few drops of distilled water and an equal amount of drinking water are placed upon watch glasses and evaporated side by side upon a hot plate, it will be found that the pure water leaves no residue, whereas in the case of the drinking water a distinct ring remains upon the watch glass, and this ring is composed of solid substances which were held in solution. Moreover, pure distilled water tastes quite differently from spring water. We are even inclined to say that the latter has no taste and that the taste of the former is unpleasant. This is because

we are accustomed, in our everyday life, to drinking water that has not been distilled and which is in reality a dilute solution of various earthy substances. Its taste, therefore, seems normal to us and that of the distilled water is unusual. If the same amount of foreign substances were added to distilled water, it would taste the same as our ordinary drinking water.

In the laboratory, distilled water is always used for chemical purposes. Spring water will introduce a certain amount of foreign substances which would exert characteristic effects that would have to be taken into consideration in carrying out the different experiments. For this reason it is desirable to use water having no foreign substances dissolved in it. In the case of chemical industries, however, the cost of distilled water has to be considered, and in many cases it is very necessary to obtain a natural water which is as pure as possible. The purest natural water is rain water, in case it has been carefully protected from contamination by any foreign substance; still this source of water is irregular and hard to collect in desired quantities.

The process of distillation is applied not only to water but also to the purification of countless other substances. The invention of distilling apparatus was, therefore, a very important matter for the development of chemistry, for only in this way was it possible to procure many substances in a pure state. The importance of this invention (the inventor is not known) has been regarded so highly that the old distilling apparatus, the retort, has been taken as the symbol of chemistry.

**59. The heat of vaporization.** — In the transformation of substances from the liquid to the gaseous state heat is absorbed in the same way as in the transition of a solid to a liquid, and in fact the consumption of heat is greater in the former case than in the latter. This quantity of heat may be measured, in the case of water, by conducting steam into a beaker containing water which has been weighed carefully. The rise in temperature is noted, and the weight of steam,  $d$ , is determined by the increase in weight of the beaker and its contents. Let  $x$  represent the quantity of heat liberated by 1 g. of steam in passing into the liquid state,  $w$  the weight of water originally present in the beaker,  $w + d$  the

weight after some steam has been condensed,  $t_1$  the temperature of the water originally in the beaker, and  $t_2$  the temperature after all the steam has been introduced. Then in transforming  $d$  grams of vapor into water at  $100^\circ$   $dx$  calories were liberated; moreover in cooling  $d$  grams of water from  $100^\circ$  to  $t_2^\circ$  there were given up to the other water  $(100 - t_2) \cdot d$  calories of heat. The original water on its part has taken up  $w(t_2 - t_1)$  calories (*cf.* p. 40). These two quantities of heat are evidently equal, and from the equation  $dx + (100 - t_2)d = (t_2 - t_1)w$  the value of  $x$  may be computed. The true value is 540 calories, although in such

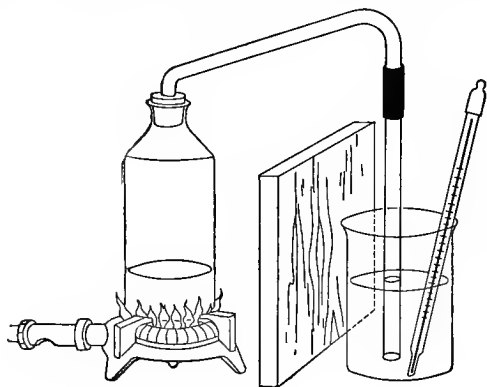


Fig. 25.

an experiment as the above a slightly lower value will be found. Special precautions are necessary to avoid all sources of error.

In this way, therefore, the quantity of heat liberated by the condensation of a vapor to a liquid may be determined. The quantity of heat required for the formation of vapor from liquid water is the same but of opposite sign; heat in this case is not set free, but disappears. The fact that the two quantities are equal and of opposite sign can be deduced from the same considerations as outlined on page 42.

**60. Steam heating.** — The large amount of heat which steam contains compared with water at the same temperature lies at the basis of a very extensive and important practical application

of steam, namely for heating purposes. Whereas 1 g. of water on being cooled from  $100^{\circ}$  to  $20^{\circ}$  loses only 80 calories of heat, it is a fact that 540 calories of heat are liberated in the condensation of 1 g. of steam to water of the same temperature, and hence  $540 + 80 = 620$  calories would be liberated during the transformation of 1 g. of steam at  $100^{\circ}$  to the same weight of water at  $20^{\circ}$  C., or nearly eight times as much as in the first case. Steam is especially well suited for transferring large quantities of heat from one place to another without the necessity of transporting large amounts of substance. On account of this property steam is used not only for heating buildings but also as a source of heat for other purposes in large chemical factories. Where the admixture of the "condensation water" is not objectionable, the steam may be conducted directly into the liquid which it is desired to heat. Otherwise, the liquid is heated by a coil of piping placed in the space to be heated.

The temperature at which steam is formed from water is not necessarily  $100^{\circ}$ , but it depends upon the pressure under which the water boils. The pressure also determines the temperature at which steam is condensed to water. Under a pressure of two atmospheres (*i.e.*, one atmosphere in excess over the ordinary pressure) the boiling point of water is  $121^{\circ}$ , and for two atmospheres of excess pressure the boiling point is  $134^{\circ}$ ; these temperatures are obtained when working with steam under such pressures. There is a certain advantage in thus being able to obtain a perfectly definite temperature which is not exceeded at any point in the heating apparatus, whereas, when a free flame is used, the parts immediately in contact with the flame are inevitably much hotter than other parts. A great many chemical substances experience change when subjected to a high temperature; when, therefore, it is desired to avoid such changes, steam has great advantages as a source of heat. By placing a manometer, or pressure gauge, in the piping, it is possible to determine at once the highest temperature prevailing in any part of the steam.

Ordinarily the piping is arranged so that the condensed water flows back into the boiler, where it is again converted into steam.

One and the same quantity of water, therefore, serves for the transference of unlimited quantities of heat.

**61. Separation by volatilization.** — Just as it was found possible to separate two solid substances by melting one of them and allowing it to flow off, so is it possible to separate a mixture of a solid and a liquid by allowing the latter to evaporate. If one substance is transformed into vapor at a temperature at which the other substance has no appreciable vapor pressure, then it is only necessary to bring the liquid to such a temperature and then the separation takes place of itself. The greater amount of space required to contain the vapor accounts for this spatial separation.

The process is a very common one when the volatile constituent is water. The "drying" of all wet or moist objects comes under this head. In chemical operations substances are frequently obtained from aqueous liquids by crystallization, or by precipitation, and they are then always moist with water which must be removed. Since water even at room temperature has an appreciable vapor pressure, it is often possible to dry such objects by simply letting them stand in the room, taking the precaution to cover them with filter paper so that they will not become contaminated with dust. The paper permits the passage of water vapor through it, and does not interfere with the drying.

Inasmuch as the vapor pressure of water increases rapidly with rising temperature, the drying will take place more rapidly in proportion as the temperature is high. Thus in chemical factories the products are dried quickly in hot closets. This requires, to be sure, a certain expenditure of heat, but it is often economical to dry in this way, as otherwise a great deal more room would be required if the same quantities of substances were handled at the same time, to say nothing of the time that would be lost in waiting for the drying to take place at room temperature. It is for this reason that drying at ordinary temperatures is employed only in the case of objects which are not very expensive and which do not require much attention, as in the manufacture of bricks. In factories there is usually enough



heat available from exhaust steam, so that the drying is really attended with very little expense.

To illustrate the separation of two substances, both solids in the original condition, by means of volatilization, we may consider the separation of sulphur and sand, a mixture which, as we have seen (p. 44), can be separated by liquefying the sulphur. If a mixture of sulphur and sand is placed in a small retort and heated, the sulphur melts and subsequently boils; the dark brown vapors of sulphur distill over, while the sand remains behind. In this case it is not necessary to use a condenser, because the boiling point of sulphur lies so high that the vapors are condensed completely by the air. The liquid sulphur flows from the neck of the retort and collects in the receiver in a pure condition. This process is also used technically on a large scale for freeing the crude sulphur from particles of sand that have flowed off with it.

In the same way, by heating a mixture of mercury and sand in a test tube, the mercury is volatilized and in a characteristic way collects upon the upper part of the tube in the form of a gray deposit. As long as the quantity of mercury is small, the drops are so tiny that they can be recognized only by means of a magnifying glass; subsequently they become larger and form a mirror-like coating at certain places on the test tube.

**62. Similarity between melting and boiling.** — The two processes by which the form of substances is changed are very similar to each other, and it is easier to remember and to apply the laws that govern them if the similarity is thoroughly understood.

In the first place, both transformations take place at a definite and constant temperature which is independent of the amount of material present. Neither the quantity of water nor the quantity of ice influences the melting point, and similarly the amount of liquid water and of steam has no effect upon the boiling point. This is one of the essential reasons why these two temperatures are made respectively the  $0^{\circ}$  and  $100^{\circ}$  points of the thermometric scale. The only condition which must be fulfilled in order to determine this temperature accurately is, in the case of melting,

that pure ice is present, because substances in solution lower the melting point. The boiling point, likewise, depends upon the same condition, only in this case dissolved substances *raise* the boiling point; here, however, the pressure must be taken into consideration, as the boiling point varies with the pressure. This leads to the question, Does not the melting point likewise vary with the pressure?

The answer is: Yes, it does; but the influence of the pressure is so slight that it required particular precautions to discover it. Our ordinary thermometers are by no means sensitive enough to detect the variations of the melting point with ordinary changes of atmospheric pressure, although they readily show the changes in the boiling point because the influence of the pressure upon the latter is much more pronounced. This is due to the fact that in the melting of ice the volume of water varies but little (about one-tenth), whereas steam occupies about 1400 times as much space as the water from which it is formed.

A second similarity lies in the fact that the processes may be reversed at the same temperature. The ice point is not only the solidification point of liquid water but also the melting point of solid water, or ice. Similarly, the boiling point is not merely the temperature at which liquid water is converted into steam but also that at which steam, or water vapor, is condensed into liquid water, both being under the pressure of one atmosphere. These temperatures, in other words, each represent points at which two different forms of one substance, water, coexist. The two forms are said to be *in equilibrium with each other*. At  $0^{\circ}$  ice is in equilibrium with water, and at  $100^{\circ}$  water is in equilibrium with steam.

Again, there is a similarity in the fact that the laws governing melting and boiling hold only with regard to pure substances. A solution does not have a single, unchangeable melting point nor an unchangeable boiling point; the former temperature gradually sinks in proportion as more and more of the liquid is converted into solid and the latter rises as the conversion into vapor progresses. Conversely, it is possible by means of this behavior to recognize a liquid as a solution; and a liquid which

behaves as a solution on being frozen shows a corresponding behavior on being boiled.

Separations are effected in both cases, for on freezing a solution it is usually the pure solvent which separates out first, and thereby the concentration of the dissolved substance increases in the solution. On boiling a solution it is the pure solvent that escapes in the form of vapor when the dissolved substance is not volatile. If the substance is volatile it also escapes with the solvent, but in most cases the ratio of the quantities of the two substances present in the vapor is different from that in which they are present in the liquid state, so that a more or less perfect separation can be effected.

These last principles find very extensive application in chemistry, and by their aid it is possible to prepare pure substances. When a chemical reaction takes place, the products are in most cases mixtures or solutions which must be subjected to a process of separation in order to obtain the different parts in a pure state. Thus solid substances are subjected to crystallization (p. 31), and volatile ones are distilled (p. 61).

#### § 8. SUBLIMATION.

**63. Vaporization of solid substances.** — In all the cases that have been discussed up to this point the substances were solid at a low temperature, liquid at a somewhat higher temperature, and gaseous at a still higher one. This is the most common case, although substances are known which are transformed directly from the solid to the gaseous state without passing through a liquid stage.

An example of such a substance is ammonium chloride (sal ammoniac), which is a white, salty substance much used by the tinsmith in soldering and by the electrician in battery jars. If a little ammonium chloride is heated in a test tube, it will be noticed that there soon begins to form in the upper part of the tube a white ring, which becomes heavier upon further heating, and which can be driven from one place to another by means of the flame. There is nothing to be seen between the ammonium chloride at the bottom of the tube and the ring on the side. If

the heating is continued long enough, all the ammonium chloride will disappear. The coating on the side of the tube will be found to consist of ammonium chloride. It is, therefore, changed by heating into a colorless gas, and the latter condenses upon the cold sides of the tube in the form of a solid again.

This process, whereby a solid is vaporized without first melting, and condensed into a solid again without passing through the liquid state, is called *sublimation*.

**64. Influence of pressure.** — The vaporization of solid substances is governed by the same laws as the vaporization of a liquid; this is particularly true of the vapor pressure, which is dependent upon the temperature and increases as this rises. Consequently, a solid substance will sublime at a lower temperature in proportion as the pressure upon it becomes less.

Since the melting point of a solid substance is almost entirely independent of the pressure, it is clear that it is always fundamentally possible, by diminishing the pressure, to lower the volatilization temperature of a liquid until it falls below the freezing point. If, for example, water is placed under a pressure of less than 0.46 cm., it ceases to exist as a liquid, for at the freezing point of water its vapor pressure is 0.46 cm. At such low pressures it is not possible to melt ice, for it vaporizes completely before the melting point is reached. Under a pressure of less than 0.46 cm., therefore, water behaves exactly like ammonium chloride under ordinary pressures, and on heating the ice it changes entirely into vapor without passing through the liquid state.

Similar statements can be made of all other substances. In every case there is some definite pressure below which the substance does not melt but sublimes. This pressure is evidently that of the liquid at its freezing point. If a little of some solid substance, the vapor pressure of which is not too low, is placed in a glass tube (Fig. 26), and the tube sealed after removing as much of the air as possible with a vacuum pump, the substance cannot be melted by heating the place where it rests, even al-



Fig. 26.

though it melts readily under ordinary conditions. All the heat imparted to the substance is used up in volatilizing it, and the resultant vapor solidifies again on the colder portions of the tube. Such an experiment can be carried out with iodine or camphor. If, however, the whole tube is heated, so that vapor with sufficient pressure is formed, it will then be found possible to melt the substance.

According to a general law of Nature, at the melting point the vapor pressure of the solid form is equal to that of the liquid form. If, therefore, the vapor pressures of a substance at different temperatures in both the solid and liquid states are plotted, as in Fig. 27, the two vapor pressure lines will intersect at the melting point. In Fig. 27, *a* represents the melting point and corresponds to  $0^{\circ}$  and 0.46 cm. vapor pressure. At pressures which are lower, and hence at temperatures and pressures which are less than those corresponding

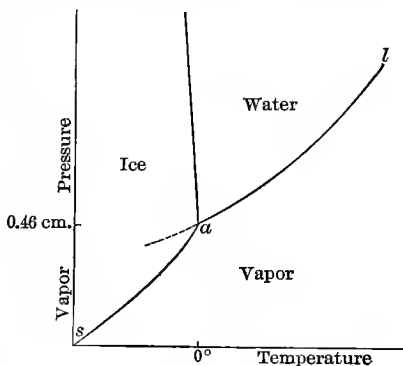


Fig. 27.

to the melting point, there is the field of sublimation, the sublimation points being represented by the line *sa*; at higher temperatures and pressures there is the field of distillation, and the boiling points of the liquid follow the line *al*.

According to this it is theoretically possible to diminish the pressure sufficiently, in the case of all substances which can be vaporized at all, to bring it within the field of sublimation. Often, however, the vapor pressure of the substance at the melting point is so extremely small that it is practically impossible to obtain and maintain such slight pressures.

## CHAPTER III.

### SOLUTIONS.

#### § 9. PURE SUBSTANCES AND SOLUTIONS.

**65. Solutions.** — From the frequently mentioned fact that every definite substance possesses certain definite properties it is possible to deduce at once a natural law, but on closer consideration we shall find that there is room for thought here. Water is, to be sure, a definite substance, and yet all its properties are not quite the same with water of different origins. Spring water has a somewhat different taste from river water or sea water. The water of the ocean not only has an entirely different taste than spring water, but its density is different, although in other respects the two kinds of water are apparently similar, for both are clear, colorless liquids, which require some special examination in order to detect the differences that are not apparent at first sight.

A liquid quite similar to sea water is obtained by adding salt to ordinary water. The salt is said to *dissolve*, *i.e.*, it disappears from sight but causes the properties of the water in which it is dissolved to change somewhat. The experiment will show that the water has become denser, for 100 cc. now weigh more than 100 g. Every one knows, moreover, that such water tastes salt.

The salt water might be regarded as a mixture of salt and water, but this is not satisfactory, because it is impossible to detect the presence of the salt with the eye. Even the strongest microscope will fail to reveal it, and if the salt was perfectly free from dirt (which is not always the case) then the salt water is also perfectly clear. If turbid, it should be filtered (p. 24).

This salt water has likewise certain *definite* properties, like pure water, although some of its properties are different. Consequently salt water may be regarded as a substance which is somewhat similar to pure water but by no means the same.

The salt water may be mixed with pure water and in this way a homogeneous liquid obtained with properties intermediate between those of pure water and those of the original solution. It no longer tastes as salt as before, and its density is nearer that of pure water. In a similar way it is possible to prepare countless substances which are not really mixtures and yet resemble mixtures inasmuch as the constituents, salt and pure water, may be mixed in a great many different proportions. All these differ slightly from one another, and if it were attempted to examine and describe them all there would be even in this simple case no end to chemistry.

Such substances as these, prepared with varying proportions of the components, are called *solutions*. They are always homogeneous substances, there not being the slightest indication that one part is different from another, and each solution has its own characteristic properties. Solutions may be prepared not only from salt and water but from all possible liquids and solids, as well as from gases. Thus sugar, saltpeter, and copper vitriol dissolve readily in water, resin dissolves in alcohol, fat in benzin. Gases are also dissolved in clear spring water, for if the water is heated or allowed to stand in the room, these gases separate out on the walls of the glass in the form of little round bubbles; the water "sparkles." This is more marked in the case of the so-called "soda water."

Liquids may dissolve one another; thus alcohol dissolves in water, and benzin in oil. All such solutions are clear, perfectly homogeneous liquids which behave like substances with definite properties.

**66. Freezing of solutions.** — In certain respects, however, solutions differ very markedly from the pure substances of which they are composed. We shall study these very important differences first with the substance best known, namely water.

We have learned already that pure water freezes at  $0^{\circ}$ . Take about 10 cc. of pure water in a test tube, *i.e.*, a round-bottomed, narrow cylinder of fairly thin glass, and place a thermometer in it. Then make a freezing mixture of ice and salt and place it around the test tube so that the water in it freezes. It is best

to introduce a small piece of ice into the water when the temperature is near the zero point, so as to prevent supercooling (p. 38). Allow more and more ice to form, and notice that the thermometer remains stationary at  $0^{\circ}$ ; we have learned that the transition of water into ice takes place completely at  $0^{\circ}$  (p. 37).

It is quite different with salt water. Dissolve about 5 g. of salt in 95 g. of water (making a five per cent salt solution), place some of the solution in a test tube and surround it with a freezing mixture of cracked ice with about half its weight of powdered salt. The solution will begin to freeze at about  $-3^{\circ}$ , a lower temperature than in the case of pure water. Furthermore, during the freezing the temperature falls continuously, and even at the last some of the liquid remains unfrozen because the freezing mixture does not lower the temperature enough to cause all the salt water to freeze. Now on removing the test tube from the freezing mixture the partly frozen salt water begins to melt, but the temperature does not remain constant, as with pure water, until all the ice has melted, but it rises gradually until as the last of the ice melts the thermometer registers  $-3^{\circ}$ , or the temperature at which the freezing began.

**67. Pure substances and solutions.** — We may study in this way all possible homogeneous substances and find that they belong either to the class which has an unchangeable melting and solidifying point or to the other class in which the solidification temperature sinks lower and lower as the freezing progresses, and the melting temperature changes in the reverse manner.

Substances belonging to the first class are called *pure substances*, those of the second are known as *solutions*.

Chemistry deals chiefly with the properties of pure substances. To be sure we shall have much to do with solutions, but, for the most part, these are used for determining in a definite way the behavior of the pure substances of which the solutions are composed. In the following pages we shall use the word *substance* to designate pure substances in contrast to solutions and mixtures.

**68. Formation and disintegration of solutions.** — A solution



is always composed of two or more substances, from which it is possible to prepare it, and into which it can be resolved. In fact, it is possible to obtain from a solution the same substances and in the same quantities as were used in preparing it. We have found the same thing to be true with regard to changes in form of a substance, for in that case it was always possible to obtain readily the same amount of the original form again. Whereas in the case of changes in form it was only necessary to change the temperature, in the case of solutions it is necessary to resort to a different method if it is desired to obtain the original substances. In changes of form, one form passes completely into another and there is not any separation involved when it is desired to obtain the original form. With solutions, however, there are always at least two different substances present and a special procedure is necessary in order to separate these constituents.

In the last of the above experiments such a separation was involved. Seafaring people are well acquainted with the fact that fresh water is obtained by melting the ice that forms upon salt water. In freezing a solution, usually one constituent separates out first as a solid in a pure state.

This is also the reason why the temperature constantly becomes lower as a solution freezes. It can be readily shown by experiment that the freezing point of a salt solution, not too concentrated, is lower in proportion to the amount of salt it contains. If, now, it is pure water that first separates out when a salt solution freezes, then the amount of water remaining in solution is smaller than before, although the quantity of salt remains the same, so that the solution becomes more concentrated, as the ice forms. Consequently, the temperature must fall still lower before more ice will form. And so the process goes on up to a certain point, with the temperature falling lower and lower as fresh portions of ice are formed.

In the case of pure water it is quite different. If a part of it has solidified, then it is still pure water that remains and there is no reason whatever why the freezing temperature should change. The freezing point remains constant until the last drop of the pure water has frozen.

The question now arises, Is this peculiarity with regard to the freezing point common to all solutions? The answer is, Yes. There are, moreover, quite a number of other properties that are common to all solutions. If, therefore, a substance which is not a mixture has one of the properties of a solution, it may be expected that it will show the other properties also.

**69. Solution and fusion.** — The solution process consists, in the above case, in bringing a solid substance into a liquid, with the result that everything becomes fluid. In this respect solution is comparable to fusing or melting, which consists, as we have seen, in making a solid substance liquid. There is one important difference, however, namely, that it is not necessary to raise the temperature. There is another similarity in the fact that when a substance is dissolved there is usually an absorption of heat, as is shown by the fact that the liquid becomes colder. If water and finely powdered potassium nitrate, both at the room temperature and in the proportion 5 : 1, are brought together and stirred with a thermometer, the temperature will fall about 10 degrees.

The process of solution is characterized as a chemical one in so far as the properties of the dissolved substance are changed, for it passes from the solid to the liquid state. Still in general it is not hard to recover the substance in solid form from the solution. It is only necessary to remove the solvent. This takes place most readily when the latter is volatile, *i.e.*, when it is easily converted into vapor; the vapor escapes and the solid substance remains behind. In such a way, for example, common salt is obtained from salt water, or "brine," as it occurs in nature. The water is allowed to evaporate and the salt is kept behind. The evaporation takes place first of all in the air and later by heating, whereby the water is driven off more rapidly and more completely.

**70. Solubility.** — Whether a solid substance dissolves or not, depends both upon its own nature and upon that of the solvent. In general, it may be said that a solvent can be found for every substance, *i.e.*, a liquid in which it will liquefy and dissolve: as a rule there are many such solvents. Conversely, for every liquid

there are certain substances which will dissolve in it. But there are also many substances which will not dissolve in a given liquid. In such a case the solid is said to be *insoluble* in the liquid, and the liquid is not a *solvent* for the solid.

Thus common salt and saltpeter dissolve in water but are insoluble in oil or in benzin. Resin, on the contrary, dissolves in alcohol and in benzin, but does not in water. In textbooks of chemistry the solubility relations of each substance mentioned are described.

Liquid solutions may be prepared not only of solid substances and liquids but also from two or more liquids, and similar differences are found with regard to the solubility of one liquid in another. Thus alcohol dissolves in water and forms a homogeneous liquid in which the two constituents are not distinguishable from one another. On the other hand, oil does not dissolve in water, and if, by shaking, it is attempted to mix these two liquids thoroughly, an emulsion is formed (p. 26) consisting of tiny drops of oil floating in the water. Under the microscope these droplets of oil are easy to recognize. After some time the lighter oil rises and collects on top of the water, so that two layers of liquid are formed. From this it follows that oil and water merely form a mixture and do not dissolve in one another. The opacity of the emulsion also betrays it to be of the nature of a mixture (p. 19).

Finally, gases also dissolve in liquids. All water that has stood in contact with the atmosphere contains dissolved air, and, if the water is heated, the dissolved gases are expelled and collect in bubbles on the side of the vessel. This takes place before a temperature of  $100^{\circ}$  is reached, at which point bubbles of steam are formed.

**71. Evaporation of solutions.** — The laws deduced on page 49, with regard to the formation of vapor from liquids, hold true with pure substances; solutions behave differently in several important respects.

If an aqueous solution of a substance, such as saltpeter, is heated to boiling, it will be found, in the first place, that the boiling point is higher than that of pure water. It depends upon

the concentration of the solution and is higher in proportion to the salt content. The boiling point rises about  $0.1^{\circ}$  for each per cent of saltpeter present, so that a ten per cent solution boils at  $101^{\circ}$ .

Then it will also be found that the solution does not have a permanent boiling point; for, during the boiling, water is constantly escaping as steam, while the saltpeter remains behind. There is therefore relatively more saltpeter in the remaining solution than before, and hence the boiling point rises.

A similar behavior takes place with all other solutions, except that the influence of the dissolved substance upon the boiling point varies with the nature of the dissolved substance. Common salt has about twice as much effect as the same weight of saltpeter; the boiling point rises about  $0.2^{\circ}$  for each per cent of salt present.

Solutions behave similarly on boiling, therefore, as on freezing, except that the temperature changes in the opposite direction; on boiling it constantly tends to become higher, on freezing to become lower. The cause of this change is the same in both cases, for water is removed from the solution whether ice is formed or steam escapes, and the solution thereby becomes more concentrated. Hence solutions may be recognized and distinguished from pure substances by studying the behavior on boiling or on freezing; if a liquid behaves as a solution in one case it will in the other. If, on the other hand, solutions of different substances are prepared, they always behave on boiling or freezing so that the temperature changes during the process and there is at the same time a separation into the constituents.

**72. Solutions of volatile substances.** — When both components of a solution are volatile, or capable of being converted into vapor, the behavior on boiling is somewhat more complicated. All that has been said above was limited strictly to the case where the dissolved substance was not converted appreciably into vapor at the prevailing temperatures. Naturally the separation does not take place so readily when the vapor of the dissolved substance is mixed with that of the solvent.

That in such cases it is possible to effect a more or less perfect

separation, depends upon the fact that the vapor in general has a somewhat different composition from that of the original liquid. The best-known example of this case is the solution of alcohol in water which is obtained by fermentation, and from which alcohol is obtained in the distillery. Pure alcohol boils at  $78^{\circ}$ , whereas water boils at  $100^{\circ}$ . If the solution of these two liquids is brought to boiling the vapor will consist largely of alcohol mixed with a certain amount of water, the proportion of alcohol to water being greater than that of the original solution. There remains behind a liquid containing more water in proportion to the alcohol. Thus, to be sure, a partial separation takes place.

To control this process it is necessary to make use of some means of quickly estimating the quantity of alcohol present in solution. Since the density of water is 1 and that of alcohol is 0.794, the density of alcoholic solutions will have an intermediate value, and by determining the density the amount of alcohol present can be estimated. As an experiment, prepare a solution from one part of alcohol and two parts of water and distill off about one-half, using the apparatus shown in Fig. 23. Then determine the density of the distillate and of the residual liquid in the flask (after cooling to  $15^{\circ}$ ). The density of the distillate will be found to be considerably less than that of the undistilled liquor, showing that the distillate consists largely of alcohol.

By repeating the distillation over and over again, the separation is made more complete. In practice, special stills are constructed for this purpose, making use of the principle of counter-currents, so that alcohol of high purity is obtained by distilling liquids of low alcoholic content, with the least possible expenditure of time and fuel.

**73. Separation by solution.** — The solution process may often serve for easily separating a mixture into its constituents when other methods prove unsatisfactory. The mixture is placed in contact with a liquid which dissolves one constituent but does not dissolve another. Hereby the soluble portion goes into solution and can be separated by settling or filtering as described on page 22.

Thus, for example, gold is obtained from gold-bearing sands in which the gold is present in a too finely divided condition to be separated by panning. The gold is dissolved by liquid mercury, in which the sand itself is insoluble. It is, to be sure, then necessary to separate the gold from mercury. This is done by distillation as described on page 56. Mercury boils at  $356^{\circ}$ , at which temperature gold is not at all volatile. The mercury is, therefore, distilled from iron retorts, and the gold that was in solution remains behind. The distillate is collected and used again for dissolving more gold from fresh sand.

In much the same way pure sugar is obtained from the sugar beet. The sliced beets are treated with water, which dissolves out sugar from the cells; after suitable purification, the sugar solution thus obtained is filtered, concentrated by evaporation, and pure sugar obtained by crystallization. The beets contain other substances than sugar, so that all the water is not removed by evaporation, but enough is left to keep back nearly all the impurities in the mother liquor (molasses).

There are innumerable other cases where the same sort of a process finds practical application. As an experiment, treat some black gunpowder with water and filter. Then evaporate the colorless filtrate in a glass evaporating dish (or watch glass); long, colorless crystals of saltpeter are obtained.

Since gunpowder is a mixture of saltpeter, sulphur, and charcoal, it is evident that the residue upon the filter must contain sulphur and charcoal. The former, although insoluble in water, will dissolve in another liquid called carbon bisulphide, which has a disagreeable odor, is very volatile and very inflammable. It must not be used in the vicinity of a free flame. If, after drying the residue, it is shaken with a little carbon disulphide, and then filtered, the carbon disulphide will evaporate quickly by simply allowing it to stand, and the sulphur will remain behind in the form of yellow crystals.

To effect a complete separation by means of solution, it is not sufficient merely to let the solution pass through the filter, for a part of the solution will always remain adhering to the residue and to the filter. After the solution has all run through,

therefore, some fresh solvent is poured upon the filter and residue and the washing is continued, as described on page 25, until all the soluble substance has been removed. Except when the residue undergoes change by exposure to the air, the rule to be followed in washing is not to pour fresh liquid upon the filter until the previous liquid has drained completely. In this way the washing is effected more speedily and with the least quantity of solvent.

#### § 10. SATURATION AND SUPERSATURATION.

**74. Saturated solutions.** — If to a given amount of water more and more salt is gradually added, the first portions will dissolve, forming a homogeneous solution. The dissolving of the salt, however, does not take place indefinitely, but soon a point is reached where the liquid will not dissolve any more, so that any further additions of salt will lie at the bottom of the liquid in an unchanged condition. This point is reached when 36 parts of table salt are present in 100 parts of water at room temperature. If at the start 100 parts of water and 45 parts of salt are taken, and the two are shaken together for a long time, at the end 9 parts of salt will remain undissolved. It is perfectly immaterial how great an excess of salt is taken, 100 parts of water at room temperature will never dissolve more than 36 parts of salt. A solution incapable of dissolving any more of a given substance is said to be a *saturated solution*.

Every solid substance capable of dissolving in a liquid forms with it a saturated solution when a definite relation is reached. The amount required to make the solution saturated depends upon the nature of the solvent and of the dissolved substance and shows all sorts of variations in different cases. Thus, most substances which appear to be insoluble will be found, upon very close examination, to have a very slight solubility, and a given substance will dissolve readily in one liquid and scarcely at all in another. These relations are very important in the study of chemistry, because most chemical work is not carried out with pure substances but with solutions. This is because dissolved substances usually influence one another more readily and more quickly than do pure substances; in fact, the older chemists used

to assert that substances acted only when in the dissolved state (*corpora non agunt nisi soluta*). This is, to be sure, not entirely true, but often applies.

**75. Influence of the temperature.** — The solubility relations are usually influenced greatly by the temperature of the solvent. In the case of ordinary table salt, however, this is scarcely true, since hot water will dissolve but little more than cold. Most other substances, on the other hand, show great differences. Usually more of the substance is dissolved in proportion as the temperature of the water is higher.

A substance which is much more soluble in hot water than it is in cold is saltpeter. If powdered saltpeter (potassium nitrate) is added in small portions to cold water, it will be noticed that the first portions dissolve, but that it requires less saltpeter to form a saturated solution than was true in the case of table salt. If now the solution with the excess of saltpeter at the bottom of the beaker is heated, the solid will disappear and a clear solution will result, and considerably more of the solid can now be added before the solution is saturated at the higher temperature.

If the hot, saturated solution is allowed to cool, the water can no longer hold in solution the quantity of saltpeter which it dissolved at the higher temperature, and the excess will separate out in the solid form. Let us, therefore, divide the hot, saturated solution into two parts, and cool one portion quickly by placing the beaker in cold water, and stirring the solution in it so that every part comes in contact with the cold walls of the vessel; saltpeter separates out in the form of a white, fairly fine powder. Then, when the mixture has become quite cold, the solid may be removed from the saturated solution by filtration. The solid thus obtained is not perfectly pure, for it is still wet with adhering solution. The greater part of the moisture may be removed by taking the paste, which has been drained as much as possible, and placing it upon several layers of filter paper; the liquid, or "mother liquor," passes into the pores of the paper, and after some time the saltpeter will be found dry as a somewhat lustrous powder.



In the meantime the other half of the saturated solution has been allowed to cool undisturbed, and from it there has likewise been deposited a part of the saltpeter in the form of a solid. But, in place of the white powder, large bodies have been formed. They appear to be prisms, bounded on all sides by plane surfaces, and are, therefore, recognized as crystals (p. 32). Just as most substances on passing from a molten to a solid condition assume a crystalline form, so they appear as crystals when deposited from solutions. This is true not only when a saturated solution is cooled, but crystals may also form if the solvent is removed by evaporation. If water is withdrawn from a saturated solution, a corresponding amount of the dissolved substance must be deposited; if the withdrawal of the water takes place slowly the solid usually assumes a distinctly crystalline form. Let us now take the mother liquor from each of the above experiments and pour it into a shallow dish. To prevent contamination with dust, cover the dish with a paper, which will not interfere with the evaporation of water, and allow it to stand. After a few days the volume of the liquid will diminish very materially and saltpeter will be deposited in the form of distinct crystals. Remove these and lay them upon filter paper to dry; the mother liquor may be evaporated still further and more crystals obtained if so desired.

If we examine under the microscope the powder first obtained, we shall find that it also is composed of crystals. They are, however, very small, because during the rapid cooling and stirring the crystals first deposited were allowed no time to grow into larger crystals; instead of this, more and more crystals were constantly being deposited. Thus the size of crystals depends upon whether the deposition of the solid takes place slowly and quietly or rapidly with stirring; consequently, in factories where large quantities of liquid are worked with, much larger crystals are obtained because the cooling of the larger volumes naturally takes place more slowly.

The process described above is called *crystallization*. The solid substance obtained in the form of crystals is usually in a very pure condition, so that chemists who have to prepare pure

substances usually strive to obtain them in the form of crystals. If foreign matter is present in a substance which is to be purified by crystallization, it either does not dissolve and may be removed at the start by filtration (as the dirt in common salt, p. 70) or it remains in the mother liquor and is not deposited during the crystallization process. For, if only a small amount of this foreign matter is present, the mother liquor is capable of holding it in solution until after the greater part of the crystals have formed. Hence, the last batch of crystals is usually the least pure.

**76. Solubility curves.**—It is customary to represent the solubility relations existing between a dissolved substance and its solvent by a curve which is plotted as follows: The degrees of temperature are drawn to any desired scale as a horizontal distance, and at each temperature where a measurement of solubility was made, a perpendicular is erected the length of which is proportional to the amount of substance present in a given weight of solvent (usually 100 g.) when the solution is saturated; thus a millimeter in a horizontal direction may represent  $1^{\circ}$  of temperature, and in a vertical direction the same length may represent 1 g. of dissolved substance per 100 g. of solvent. The point at the top of the perpendicular then corresponds to a given weight and temperature. Quite a number of solubility determinations are carried out at different temperatures and thus a series of points are obtained on the drawing. By connecting these points, a curve is obtained by means of which the solubility at any intermediate temperature can be ascertained at once. This is an application of the law of continuity (p. 53). The curve is called the *solubility curve* of the given substance for the solvent in question. In the case of table salt (sodium chloride) dissolved in water, the curve takes the form of a nearly horizontal line, for at different temperatures the quantity of salt required to form a saturated solution is nearly the same; thus the perpendiculars erected at the points on the plot corresponding to the temperatures at which measurements were made are *all of nearly the same height*, and the line connecting the tops of these lines runs nearly parallel to the temperature line. In the case of

saltpeper (potassium nitrate), the amount of dissolved substance increases rapidly with rise in temperature, hence the curve rises very rapidly. The curve is about the same as the vapor pressure curves shown in Fig. 20, p. 52, so that the conclusion may be drawn that the increase in solubility per degree rise of temperature is greater as the temperature is higher. In Fig. 28 perpendiculars are erected for every ten degrees of temperature, and the distance between two adjacent points on the curve becomes greater as they lie to the right on the plot.

The solubility curve of potassium chloride is shown to be a straight line, but it rises constantly from left to right. In this case the difference in solubility as represented by two neighboring perpendiculars is always the same irrespective of the temperature. Here the solubility varies a little with rise of temperature, but the rise is uniform, so that the solubility may be said to be proportional to the temperature. The fact that the solubility is proportional to the temperature is always shown when the line is straight.

**77. Supersaturated solutions.**— When a saturated solution is in contact with undissolved solid, there exists a state of equilibrium, just as in the case of a solid in contact with its melt. In the latter case, it was found that the condition of equilibrium required the presence of *both* forms, the solid and the liquid (p. 39). With the solution there is the difference that the solid and the liquid are different substances; but the state of equilibrium is likewise dependent upon the presence of both forms side by side. Just as it is possible to supercool a fused substance by carefully excluding all traces of the solid form, so in the same way it is possible to prepare a supersaturated solution from which crystals are at once deposited if a trace of the solid substance is added.

Take 100 g. of sodium acetate and heat it with 20 g. of water; the solid dissolves, forming a solution which can be filtered, while warm, through a wet filter. It is desirable to filter at this point because commercial sodium acetate frequently contains a dust-like impurity which can be removed by filtration but will otherwise interfere with the experiment. Filter the solution into

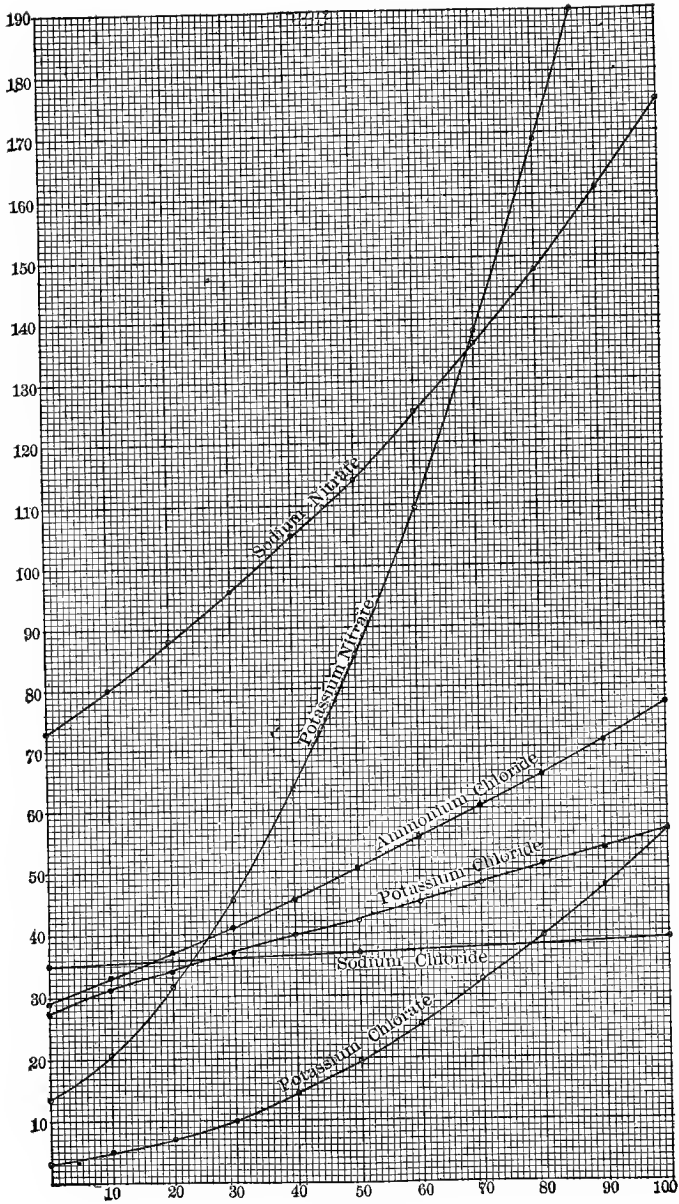


Fig. 28.

a small perfectly clean flask, and stopper the flask to keep out all dust. The liquid will keep indefinitely provided no solid sodium acetate comes in contact with it, and will not solidify even on shaking; but if a mere trace of the solid acetate is dropped into the flask crystallization takes place immediately. In fact it requires so little of the salt to produce this crystallization that if a little sodium acetate is shaken upon a piece of paper and then brushed off with a cloth as carefully as possible, enough will remain upon the paper so that a piece of it torn off from the place where the salt rested will cause immediate crystallization when introduced into the supersaturated solution. As the crystals form, the temperature of the liquid rises and the deposition of crystals continues until the remaining solution is no longer supersaturated.

The ability to form supersaturated solutions is more or less common to all substances, and there is a limit to the amount of supersaturation possible, just as it was found that there was a limit to the degree of supercooling. This limit is different with different substances.

To illustrate supersaturation with a substance less soluble than sodium acetate, take borax, of which only about 3 parts will dissolve in 100 parts of water at the ordinary temperature, whereas 20 g. will dissolve in the same amount of boiling water. Dissolve, therefore, 20 g. of borax in 100 g. of water and notice that no solid separates out as the filtered solution cools. Add finally a very little borax to the supersaturated solution and shake vigorously; at first apparently nothing takes place, but after a short time a crystalline turbidity appears, and increases rapidly on shaking.

The presence of the solid substance is so essential that the crystallization will stop after it has once begun if the solid is removed. This may be shown by an experiment with the supersaturated solution of sodium acetate. Fuse a little of the acetate to the end of a glass rod and take care that there is no loose dust upon the rod. Then dip the rod into the supersaturated solution. Immediately crystals begin to grow from all sides. After a few minutes, when the crystals are about

1 cm. long, carefully withdraw the rod with its clusters of adhering crystals but without allowing them to touch the sides of the vessel. If, in this way, all the solid is removed from the crystallizing solution, the crystallization will stop, and the liquid will remain clear indefinitely even although the solution is still strongly supersaturated.

### § 11. GASEOUS SOLUTIONS.

**78. Mutual solubility of gases.** — The name and conception of solution has up to this point been applied only to liquids, for solutions have been defined as liquids which, on the one hand, were formed from a liquid and some other substance and, on the other hand, can be separated into these constituents by boiling or by freezing; whereby the boiling and the freezing points have been found to be changeable, in contrast to the pure substances, of which both points are constant (under a given pressure).

Now there is fundamentally no objection to applying the same name to such gas mixtures as are composed of a gas and the vapors of some other volatile substance, and from which, by suitably cooling and increasing the pressure, it is possible to obtain the individual constituents. Such gas mixtures will be called *gaseous solutions* in contrast to the liquid solutions which have already been studied.

In this connection it should be mentioned, first of all, that all gases in such a sense are soluble in one another to an unlimited extent. If any two gases are mixed, there results a homogeneous solution in which no separating boundary surface is ever discernible. Thus, if illuminating gas is allowed to escape into a room, it remains invisible under ordinary conditions. The gas stream can be made visible by throwing a pencil of light rays from a projection apparatus so that it falls upon a white surface after passing through the illuminating gas. Since the index of refraction of illuminating gas is different from that of the ordinary atmosphere, the light rays are bent on passing through the gas, and a sort of shadow is cast on the screen; this is especially distinct if a narrow screen is placed in front of the projection apparatus in order to give a regular shape (tapering) to the pencil

of light. These shadows soon disappear, however, because the illuminating gas soon mixes with the air to form a homogeneous solution.

All other gases behave the same, unless new substances are formed by their interaction, *i.e.*, unless they exert a *chemical action* in the strict sense upon one another.

**79. Evaporation in gases.** — A gaseous solution may result when a gas is placed in contact with a liquid which, at the prevailing temperature, has an appreciable vapor pressure. This is constantly taking place in our daily life when for example we allow a wet object to dry in the air. An object is said to be wet when it is moist with water, and dry when the water is no longer present. Now every one knows that a wet object dries of itself by remaining in the air, only it is necessary to keep it well in contact with the air. If it is enclosed in a vessel of any kind, the object will not dry; or if it is folded a number of times, the inner parts will remain wet long after the outer portions have dried.

Drying in such cases depends upon the formation of a *gaseous solution between the air and the water vapor*. By means of the apparatus described on page 49, we can measure the vapor pressure of water vapor, which is equal to 1.5 cm. of mercury at 18° (room temperature); *i.e.*, if water is placed within an empty space it will evaporate until the water vapor in this space exerts a pressure upon it of 1.5 cm. of mercury. If the space is so large that all the water evaporates before this pressure is reached, then no liquid will remain. If the space is smaller, some of the water will remain as liquid.

When water is present in a space containing another gas (but no water vapor) the same law holds; *water will evaporate and mix with the gas until its own vapor pressure (e.g. 1.5. cm. at 18°) is reached*. The pressure of the water vapor is added to that of the other gas, so that the total pressure in the space is equal to the sum of the pressure exerted by the gas and that exerted by the water vapor.

To prove by experiment that this is true, it is better to make use of a somewhat more volatile liquid, the vapor pressure of

which is greater than that of water at room temperature. Seal a little of some such liquid (*e.g.* ether) in a thin-walled bulb and introduce it into a larger flask which is connected with a manometer (Fig. 29) to measure this pressure. When the sealed bulb

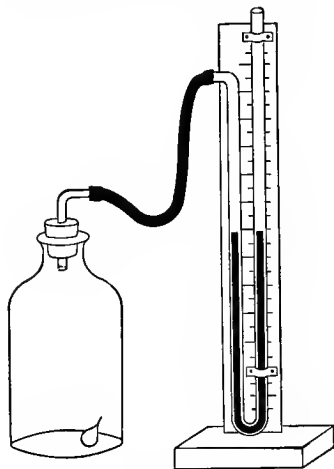


Fig. 29.

is broken by shaking the bottle, the mercury in the manometer will immediately rise. Since ether has a vapor pressure of 40 cm. at 18°, the manometer tube must be made sufficiently long to allow for it.

**80. Partial pressures.** — Volatile liquids evaporate in the presence of a foreign gas just as if the latter were not present, and the final gas pressure is simply the sum of the two pressures. To each constituent of a gaseous mixture, therefore, is assigned a partial pressure which is estimated on the basis of what it would be

if it were present alone in the space. *The total pressure of a gaseous solution is equal to the sum of the partial pressures of its components.*

**81. Water vapor in the atmosphere.** — The air that surrounds us is in contact with many water surfaces, namely those of rivers, lakes, and oceans, the last of which comprise five-sevenths of the earth's surface, so that one would think that there would be enough moisture in the air to correspond to the vapor pressure of water at the prevailing temperature. The air is said to be *saturated* with water vapor when this is true. The term has the same significance as when applied to a liquid solution which is in contact with an excess of the dissolved substance, namely, that under the prevailing conditions no more water will pass into the atmosphere. If, for any reason, there should be more water vapor present in the air, then the excess would at once separate out in the form of liquid water just as the excess of potassium



nitrate will separate out on cooling from a solution which was saturated at a higher temperature.

As a matter of fact, the air is very seldom saturated with water vapor, although this is the case during a heavy shower; usually there is only about two-thirds as much water vapor in the air as would be required to saturate it. This is because there are, under ordinary conditions, quite a number of influences acting which tend to diminish the water content of the air, and none which tend to raise the amount of water vapor above the saturation point. The chief of these influences are the temperature changes which take place in the atmosphere.

We know that the vapor pressure of water; like that of every other liquid, increases with rising temperature. Consequently, the quantity of water vapor which must be present in order to make the air in a given space saturated also increases with rise of temperature. In a cubic meter of air, the following amounts of water are required to saturate it at different temperatures:

TEMPERATURE.	WATER IN GRAMS.
0°	4.9
5	6.8
10	9.4
15	12.7
20	17.1
25	22.8

It is evident from this table that the quantity of water required to saturate the air is doubled if the temperature rises about ten degrees. If, therefore, a given quantity of air is saturated at 5° and then is heated to 15°, it could take up about an equal weight of moisture before it would be saturated at the higher temperature. In other words, the air is only half saturated at the higher temperature.

Again, if some air saturated with water vapor blows from the ocean over the land and is warmed there, this of itself serves to make such air unsaturated. - If the air is cooled, the excess of moisture separates out in the form of rain or dew, and if it is raised subsequently to a higher temperature, the air becomes unsaturated. This explains why the air out of doors, as well as

indoors, is seldom saturated with water vapor. Particularly in winter, when the outside cold air needs but very little moisture to saturate it, this air reaches a high degree of unsaturation when it comes into a warm room. Hence the air in houses during winter is often uncommonly dry, and especially when the ventilation is good; in such cases it is desirable to provide special arrangements for introducing moisture into the air and to bring the content of water vapor up to that point which is most suitable for good health.

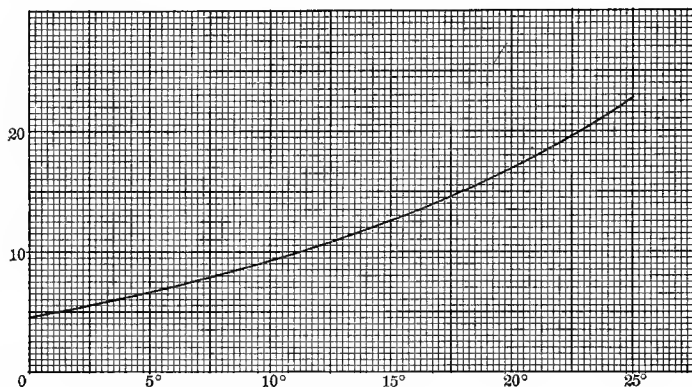


Fig. 30.

The incomplete state of saturation of the air with water vapor is also the reason why moist objects dry in the air. This does not happen when the air is saturated; in rainy weather the washerwoman cannot dry her clothes out of doors, even if they are sheltered from rain; similarly, on shipboard, objects feel somewhat moist.

The fact that water vapor is always present in the atmosphere is easy to demonstrate by merely cooling some of it. If a little ice is placed in a glass of water and the contents of the glass are well stirred, the water and the walls of the glass become cold, and moisture is deposited on the outside, as is recognized by the turbid appearance. It is sometimes said that the glass "sweats." This takes place all the more readily if the air is nearly saturated

with water vapor. Since human beings are constantly breathing out water vapor, it follows that the air where many people are assembled is rich in this vapor and is, therefore, near the saturation point. Thus a glass of cold water becomes wet on the outside very quickly when the air has been breathed by many people. Then, again, windows become quickly covered with drops of water if the outside temperature is low, and this takes place more readily in proportion as the air within is warm and moist.

By determining the temperature at which deposition of water takes place, it is possible to estimate the degree of saturation, or *humidity*, of the atmosphere. From the remark on page 89, that a rise of ten degrees in temperature doubles the quantity of moisture which the air will hold, one can assume, on the other hand, that air is only about half saturated with water vapor when it is necessary to cool a glass ten degrees before water will condense upon it. If the temperatures given in the table on page 89 are indicated on a horizontal line, and at the corresponding points perpendiculars are erected whose lengths are proportional to the corresponding quantities of water, then, by connecting the upper points of these perpendiculars, a curve is obtained (Fig. 30) which will give the quantities of water vapor required to saturate air at all intermediate temperatures. If, then,  $t$  is the temperature of a given space,  $t_s$  the temperature at which moisture begins to deposit on glass,  $d$  the amount of water required for saturation at the first temperature, and  $d_s$  that corresponding to the second temperature, then the fraction  $\frac{d}{d_s}$  is the ratio of the moisture in the air to that required for saturation, or the *degree of humidity*. It is evident, therefore, that the degree of humidity of the atmosphere can be estimated from the *dew point*. If the student carries out such a determination on a sunny day and again on a rainy day, the difference in the humidity of the air will be shown.

## CHAPTER IV.

### CHEMICAL REACTIONS.

#### § 12. CHEMICAL COMBINATION.

**82. Chemical reactions.** — If 1 g. of sulphur and 6.25 g. of mercury are heated cautiously in a long, narrow test tube, the sulphur will first of all melt to a brownish-yellow liquid, which floats upon the much heavier mercury. If the mixture is then heated a little more strongly, there is a crackling sound and a fairly violent reaction takes place whereby there is formed from the silver-white mercury and the yellow sulphur a black substance which is not volatile like the two original substances but which remains a solid even if heated until the glass of the tube containing it begins to soften. As a rule there is crackling during this last heating, because there is likely to remain in the interspaces of the new compound some residual sulphur and mercury which did not come in contact with each other during the first heating. Soon the crackling ceases, and, after cooling, the new substance may be shaken out of the tube; by a close examination it will be seen that it bears no resemblance to the substances from which it was formed. Since it resulted from mercury and sulphur, it is called mercury sulphide.

Here we meet with a phenomenon essentially different from anything that we have studied up to this point. It is in some respects comparable with the change in form; in that case, however, one substance disappeared and another took its place, whereas here two substances disappear and one is formed. This is called a *chemical combination* and it is said that mercury and sulphur have *combined* to form mercury sulphide.

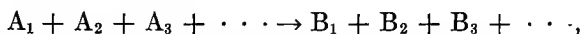
Such processes, called *chemical reactions*, are innumerable. From 16 g. of iodine, which is a brownish-black solid substance resembling graphite in appearance, and 25 g. of mercury, there

results, by simply rubbing the two substances together, a beautiful scarlet-red powder called mercury iodide; or, in other words, a new substance is formed. If 14 g. of iron and 8 g. of sulphur are ground up together, a greenish-gray mixture results from which iron can be withdrawn by a magnet and the sulphur can be extracted with carbon disulphide (p. 78). If a test tube is filled with this mixture and then heated, the mass suddenly begins to glow, the glowing spreads throughout the whole mixture, and finally, on cooling, a black mass is found which will not give up iron when brought in contact with a magnet nor sulphur when treated with carbon disulphide. It is a new substance with new properties.

A chemical change, strictly speaking (p. 28), takes place every time certain substances disappear and new ones take their places; the change may take place in nature or be brought about artificially. When charcoal or wood burns, when grape juice is converted into wine by fermentation, when iron rusts, etc., we recognize therein chemical processes.

In all such cases we can ask the following questions: What substances disappear in the process? What substances are formed?

If we designate the disappearing substances by  $A_1, A_2, A_3$ , and those that are formed by  $B_1, B_2, B_3$ , then the chemical change may be expressed as follows:



where the dots represent the fact that it is necessary to include all of the A and all of the B compounds, *i.e.*, to designate all the substances that have disappeared and all those that have been formed.

The chemical changes by which mercury sulphide, mercury iodide, and iron sulphide were formed, as described above, may all be represented by the formula



**83. Conservation of weight.** — If we recall, now, the law of conservation of weight (p. 29), we shall naturally ask ourselves whether this law still holds when these deep-seated changes

occur. As has been mentioned before, there is no known condition by which the law of the conservation of weight is influenced or disturbed in the slightest, so we may conclude that it holds in the case of chemical changes of all kinds. The most careful investigations, carried out recently with the aid of all modern appliances, have led to the conclusion that this law always holds true precisely.

In the above representations, therefore, we can go one step further and say that the designations A and B refer not only to the nature of the substances but also to their weights. For the weights of substances that have disappeared must be equal to the weights of substances that have been formed; hence the above expression can be made into an equation:

$$A_1 + A_2 + A_3 + \dots = B_1 + B_2 + B_3 + \dots$$

For example:

Mercury + Sulphur = Mercury Sulphide.

Mercury + Iodine = Mercury Iodide.

Iron + Sulphur = Iron Sulphide.

In the above cases it will be noticed that the substances formed are named after the original substances. This is to signify, in the first place, that the former can be prepared from the latter. We shall subsequently learn that the significance of these names goes further and implies as well that the original substances also can be prepared from the new ones.

The equations assert that the weight of mercury sulphide is equal to the sum of the weights of mercury and of sulphur that have disappeared. If, therefore, two of the three quantities are known, the third may be calculated by means of the equation. As self-evident as it may seem, this principle is very important in chemistry and meets with many applications. Frequently one of the substances involved in the equation cannot be weighed very easily. It is then always permissible to compute this weight from that of the other substances.

**84. Definite proportions by weight.** — For carrying out the above experiments of preparing new substances, certain specific weights were prescribed, and the question naturally arises as

to what would happen if different quantities of the substances were taken.

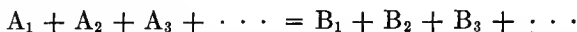
First of all, it is to be said that the process will always take place in the same way if the prescribed quantities are increased or diminished proportionately. Thus if 2 g. of sulphur and 12.5 g. of mercury were taken instead of 1 g. sulphur and 6.25 g. mercury, the result of the experiment would be precisely the same, except that twice as much mercury sulphide would be formed. The absolute quantities, or weights, of the substances employed have no influence upon the chemical process. Of course it is more convenient to work with the given quantities than with, say, 1000 times as much; the larger quantities would involve the use of larger and stronger apparatus.

It remains, then, to discuss what would happen if the weights used did not bear the same relation to one another. From our study of solutions, it might seem fair to expect that a similar compound would result but one with slightly different properties. To see what would actually happen, let us perform the following experiment. Heat 2 g. of sulphur with 6.25 g. of mercury, *i.e.*, the same quantity of mercury as used before, but twice as much sulphur. Proceed just as before and finally examine the resulting product. It will be found that black mercury sulphide is again formed but it is now mixed with unchanged yellow sulphur which has not in any way entered into the composition of the new substance. From this it follows that a given quantity of mercury will unite with only a definite quantity of sulphur and with no more. There is here, therefore, a certain kind of *saturation* involved (p. 79), just as a given quantity of water will dissolve only a certain quantity of table salt and no more. Since, however, this quantity of water can form a solution containing less salt, although the solution will have a lower density, etc., it remains for us to ascertain what would happen if more mercury or less sulphur were used in the experiment. Heat, therefore, 0.5 g. of sulphur with 6.25 g. of mercury and examine the resulting product. Again black mercury sulphide will be formed, but over it will be found a deposit of metallic mercury (p. 46), and if this is carefully brushed, with the aid of a feather, into a small

dish, and then weighed, it will be possible to recover about 3 g. of unchanged mercury. When the experiment is carried out with all possible precautions, it will be found that it makes no difference whether the mercury or the sulphur is originally present in excess, the resulting compound will always contain sulphur and mercury in the proportion 1 : 6.25 or 4 : 25; if more of either element is taken, the excess will remain unchanged and will take no part in the process.

Whereas, in the case of solutions it was possible to vary within wide limits the amounts of the substances involved, here, on the contrary, there is a perfectly definite relation between the two substances; that which is formed is, indeed, neither a mixture, nor a solution, but a *new substance with characteristic properties*.

**85. The law of definite proportions.** — The general applicability of this law has been tested in countless cases where chemical reactions take place. The law of definite proportions, as it was called by its discoverer, holds true universally. According to this, in the equation



the substances designated by A and B refer to perfectly definite ratios by weight, and if it is established that a certain number of grams of  $A_1$  take part in the process, then it can be told what weights of  $A_2$ ,  $A_3$ , etc., will be required to react with this weight of A, and also what weights of  $B_1$ ,  $B_2$ ,  $B_3$ , etc., will be formed. This holds true whether one substance is formed or several, as we shall see by a number of examples.

This important law will be understood perhaps better after the following consideration. It has been found that the properties of a compound substance are dependent on the nature of the substances from which it is formed. From given substances it is possible to obtain only products of definite properties, whether these be mixtures, solutions, or new substances. To be sure, the properties of the first two classes can be changed within certain limits corresponding to the relative weights of substances present in solution or in a mixture; if, however, the weights are determined, then so are the properties. This is so unquestion-



able that by measuring some property (*e.g.* the density) the relative amounts of substance and solvent present in a solution can be determined (p. 77).

Now pure substances have the peculiarity of always having perfectly definite properties, which cannot be changed within any limits, but always exist irrespective of how the substance may have been prepared. If, therefore, the properties depend upon the composition, it follows, as a logical consequence, from the fact that the properties of a substance are always the same, that the composition will likewise always be invariable. And this is perfectly true, as the above experiments indicated and as has been shown by a great many experiments in which exact measurements have been made. The law of definite proportions is a perfectly general law, which holds true for all pure substances (*i.e.*, for those with constant properties) and for these only. It does not apply to solutions or to mixtures, and by means of the law it is possible to distinguish pure substances from mixtures and from solutions.

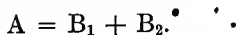
Pure substances, which can be prepared from two or more other pure substances, by chemical combination in definite proportions, are called *compound substances* or simply *compounds*.

That a combination has taken place is evident from the fact that the weight of the new substance is equal to the sum of the weights of the substances from which it is formed. The latter are called the *components*. Simple substances are those which cannot under any conditions be prepared by the union of two or more other substances. In other words, simple substances have no components.

### § 13. CHEMICAL SEPARATION.

**86. Decomposition.**—In all the above chemical reactions there was prepared from two substances a third whose weight was equal to the sum of the weights of the starting materials. One may ask whether, conversely, two substances may be formed from one. These two would then form a mixture or a solution, and it would be necessary to separate the parts from one another

in some such way as has been described in certain special cases. The equation for such a process would be



Such reactions are of frequent occurrence, although, to be sure, they do not often take place so simply and readily that it is easy to observe them. One such reaction, and one which at the same time has great historical significance, is the following.

There is a certain yellowish-red substance which can be prepared in a chemical way and is called *mercuric oxide*. If a little of this substance is placed in a thick-walled test tube and heated strongly, a number of interesting changes will take place. First, the substance becomes darker and darker and finally black. This is merely a change in color which is dependent upon the temperature, for if the substance is allowed to cool it will again assume the yellowish-red appearance. The color of the substance, therefore, depends upon the temperature, as is not unusual. If, however, the substance is more strongly heated, it becomes transformed into a gas. This upon investigation proves to be a gaseous solution; for, if the gas is cooled slightly, a gray deposit is formed upon the walls of the tube and can be recognized as metallic mercury, while a part of the gas escapes in spite of the cooling. We have already learned that a colorless gas cannot be seen. If a splinter of wood is lighted, and then blown out so that the carbon still glows somewhat, it will be found to ignite quickly if placed at the mouth of the test tube where it comes in contact with the escaping gas.

It might be thought, perhaps, that the glowing splinter ignites merely on account of the heat, but if the experiment is carried out in the same way over an empty test tube, it will be found that the splinter will not ignite even although the tube may be heated much more strongly than before. The conclusion, therefore, must be drawn that a new gaseous substance is present in the first test tube, and that this gas has the property of making a glowing splinter take fire. The gas must have come from the mercuric oxide, for there is nothing else that could cause its

presence and, moreover, some mercuric oxide has disappeared. As the experiment continues, the quantity of mercuric oxide gradually diminishes, the mercury on the walls of the tube increases, and more of the gas constantly escapes from the tube. This gas is called *oxygen*.

**87. Oxygen.** — To make sure of the presence of the oxygen, it may be collected by itself. This is easily accomplished by closing the test tube with a perforated stopper into which a glass tube is fitted so that it is air tight, having the form shown in Fig. 31. By means of rubber tubing the outlet tube is connected with another glass tube which dips under water. The tube is

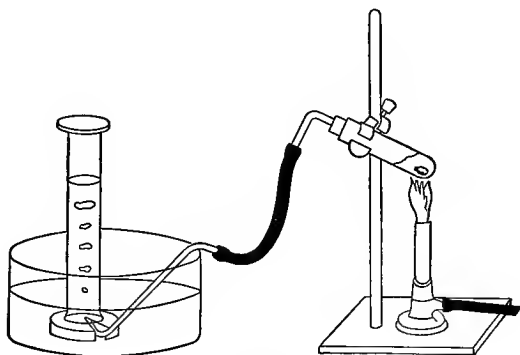


Fig. 31.

clamped in position as shown in the drawing. When the gas is evolved, the bubbles have to pass through the water, so that they can be seen and also collected.

To collect the gas, a glass cylinder is filled with water and then covered tightly with the hand or with a plate of glass. The cylinder is then inverted, and when the mouth is under water the hand, or the plate, is taken away. The water will not fall from the inverted cylinder, because it is a hydrostatic principle that the atmospheric pressure will hold up a column of water which is about 10 meters high (= 760 mm. of mercury). At first the inverted cylinder is placed at one side while the contents of the test tube are heated.

At the start only air bubbles escape, but these bubbles soon grow smaller until they almost entirely cease coming off. These are due to the fact that the air in the test tube expands on being heated. Soon, however, a regular succession of bubbles will begin to escape, and if a little of the gas is now collected by inverting a small test tube full of water over the place where the bubbles escape, and allowing them to displace the water in the tube, it will be found by the glowing splinter test that the gas is rich in oxygen. Then the larger cylinder is placed over the end of the tube, and filled with gas in the same way. When the last portion of mercuric oxide disappears from the test tube, the last bubbles of oxygen will be evolved; in this way it is shown that the oxygen actually comes from the mercuric oxide.

**88. The decomposition equation.** — Just as before, we may express the chemical change by the equation



and according to the law of the conservation of weight, the original weight of mercuric oxide is equal to the sum of the weights of mercury and oxygen that are formed. The fact that a third substance is not formed is obvious because the experiment is carried out in a closed vessel in which there is no apparent possibility of another substance being concealed.

To be sure, it were possible that some substance was given off which was dissolved by the water in the dish at the same time that the bubbles of gas arose in the cylinder. In that case, however, the liquid in the dish would not have remained water but would have become a solution, and the presence of the dissolved substance could have been detected. Experiment shows, however, that the water has remained unchanged during the experiment, so that there is no reason at all for doubting the accuracy of the above equation.

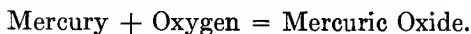
Another way of testing the equation would be to weigh the amount of oxide taken and of mercury and oxygen formed. If the first weight was found equal to the sum of the last two weights, then there would be no possible ground for

doubting the equation, for it is inconceivable that a substance would be formed which has no weight.

Chemical reactions, as we have already learned, in which one substance is formed from two or more other substances may be called processes of combination, and the substances formed are known as compounds, while the original substances are components. Mercuric oxide is a compound of sulphur and mercury.

Chemical reactions in which two or more substances are formed from a single homogeneous substance are called *decomposition processes*, and the substances formed are *decomposition products*. Mercury and oxygen are the decomposition products of mercuric oxide.

**89. The reversibility of chemical reactions.** — One may ask whether, conversely, it is not possible under proper conditions to form the original substance from the decomposition products, in which case the equation would read



The answer is that this is perfectly possible. If mercury is very cautiously heated in a stream of oxygen gas, at a temperature such that the metal is just ready to boil, a combination will take place, the mercury with some of the oxygen will disappear and mercuric oxide will be prepared of exactly the same properties as the sample which gave up mercury and oxygen on being heated to a higher temperature. Unfortunately, the process takes place very slowly, so that it requires several days to obtain a very small quantity of mercuric oxide in this way. It is, therefore, not suitable for a simple laboratory experiment.

On the other hand, if we take another example, it is very easy to study this reversibility of chemical reactions. There is a well-known copper salt called blue vitriol. If some of this copper salt is coarsely powdered and then heated in a small retort upon a sand bath, a film of moisture will deposit in the neck of the retort and water will collect in drops and run off. A flask, as receiver, may be placed in front of the retort and the experiment continued at a gentle heat until finally no more

water is given off. The receiver is kept cool, to condense the steam, by placing it in a dish of cold water (Fig. 32), or by the method described on page 56. It is well to cover the upper part of the retort with asbestos paper, for if the walls are so cold that steam condenses upon them, this water may fall upon the hotter bottom of the retort and break the glass.

At the end of the heating, a grayish-white mass remains behind, and water will have passed over into the receiver.

If now the retort and its contents are allowed to cool, then, upon pouring the water in the flask back into the retort, the water will disappear and the blue color will reappear. The blue

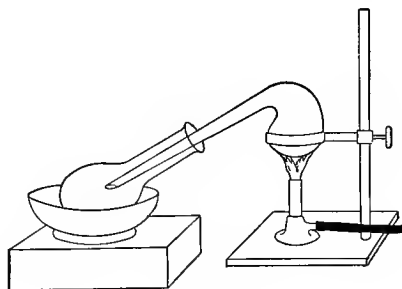
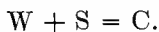


Fig. 32.

substance, which is again copper vitriol, appears to be perfectly dry. If we call the blue substance C, the white substance S, and the water W, then when the water was driven off and the white substance formed, the process may be represented by the equation

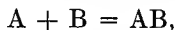


and when the blue substance was formed again



Between these three substances, in other words, it is possible to accomplish a decomposition as well as a combination, and from the decomposition products the original substance can be formed again.

From this we are in a position to understand another important law, namely, that combination and decomposition are reversible processes. If from the constituents A and B a compound substance C can be prepared, then from the compound C it is possible to obtain the components A and B. Sometimes this cannot be accomplished easily or directly, but there is some way in which it can be done, and it is always the same substances A and B that are obtained. Moreover, it is not alone the same substances that are obtained, but they are obtained in the same relative quantities, namely, in the same proportions as those in which they united originally to form the compound substance. Consequently, it is simplest not to give to the compound C an arbitrary designation, but rather to name it so that it is at once evident that it can be prepared from or decomposed into the constituents A and B. In chemistry it has become customary to designate the compound as if it were a mathematical product, and thus to the substance composed of A and B the name AB is given. The equation for such a chemical process, therefore, may be written



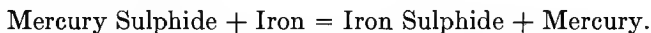
and the assumption is made, in accordance with the mathematical use of the equality sign, that the equation may be reversed, thus:



and this is right and proper, as experiment has shown.

**90. Indirect decomposition.** — It has been stated above that the component parts of a compound can be prepared from it even although an indirect process may sometimes be found necessary. For example, the black sulphide of mercury which has been prepared in a previous experiment does not have the property of decomposing into mercury and sulphur on being heated. If the experiment is carried out and some of the sulphide is heated strongly, it is quite true that it does not remain absolutely unchanged; but the only thing that happens is that it volatilizes and deposits in the upper colder portions of the tube. Mercury sulphide, therefore, is volatile at a high temperature, but remains the same compound.

Now, however, let us mix some of the compound substance with a little iron powder and repeat the experiment. It has been found experimentally (page 93) that iron will combine with sulphur, and it will be remembered that it was necessary to heat the mixture more strongly than in the preparation of mercury sulphide. It is conceivable that the sulphur (which can be obtained from the sulphide of mercury) would prefer to combine with iron rather than with mercury. As a matter of fact, it is not necessary to heat the mixture of iron and sulphide of mercury very long before the well-known gray deposit of mercury is obtained in the upper part of the test tube. The following reaction has taken place:



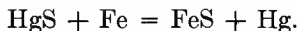
The chemist does not usually write out the full name of each substance but makes use of abbreviations, which in this case are as follows:

S = sulphur; Latin, *sulfur*.

Hg = mercury; Latin-Greek, *hydrargyrum*.

Fe = iron; Latin, *ferrum*.

The equation representing the chemical reaction is usually written



This kind of a reaction is evidently of a different nature from any other that we have studied. In the previous cases two substances, and only two, have united to form one compound, or, conversely, the two elements have been obtained from the one compound. Here we have made use of a third simple substance which acts upon a compound of two others in such a way that it combines with one and sets the other free. We say that the iron sets the mercury free, for in the compound the mercury is regarded as combined, or bound, because it is not possible to recognize in it the characteristic properties of mercury. Of all its properties, only that of weight remains.

Another way of looking at this has been to say that the iron has "driven out" the mercury from its compound owing to the fact that the iron is assumed to have a greater "affinity"



for the sulphur. Chemical processes of this nature, therefore, have been called decompositions by *selective affinity*. This last expression is obviously too narrow, because a combination takes place side by side with the decomposition. Such reactions, however, are usually employed for the purpose of obtaining the substance set free, and consequently the chief weight is laid upon the fact that the element is set free from its compound.

**91. Identification of the substance formed.** — It remains still to identify the substance that results from the action of iron upon sulphide of mercury, and to prove that it is actually the sulphide of iron and not some other substance. Inasmuch as the sulphides of both iron and mercury are black in color, it is necessary to seek for some other means of distinguishing between the sulphides of iron and mercury.

It is possible to apply a test in which the sense of smell is utilized. Let us take some of the sulphide of iron that was prepared directly by the combination of iron with sulphur, and pour over it a little hydrochloric acid. Hydrochloric acid solution is a colorless transparent liquid which exerts a very strong chemical action in various ways, as we shall soon learn. In this case we make use of it merely to bring about a certain reaction with sulphide of iron which is characteristic of this compound; the chemist usually says that hydrochloric acid in such a case serves as a *reagent* in testing for sulphide of iron. Dilute acid is used, *i.e.*, acid mixed with water, so that the action will not be too violent. At the mouth of the test tube, the odor of rotten eggs will be detected. This is due to the presence of a gas, called sulphuretted hydrogen, or hydrogen sulphide, which is evolved by the action of dilute hydrochloric acid upon sulphide of iron. It is not necessary at this place to study this reaction further; it suffices here to know that when sulphide of iron and hydrochloric acid are in contact with one another, the odor of rotten eggs results.

If, now, dilute hydrochloric acid is poured upon the residue obtained by the heating of sulphide of mercury with iron, the odor of rotten eggs is at once noticeable. This indicates that the residue

is sulphide of iron, or at least that it contains some of this compound.

To be sure, a certain objection may be raised. Perhaps the sulphide of mercury also gives the odor of rotten eggs when it is treated with dilute hydrochloric acid. It is very easy to decide this point by trying the experiment of pouring a little hydrochloric acid upon some sulphide of mercury. In this case the odor is not obtained. Similarly, the odor of rotten eggs is not obtained, or at least not to any extent, on treating iron with hydrochloric acid, although there is effervescence, *i.e.*, a gas is set free and it has an unpleasant odor. Of all the substances present, or which might possibly be present, it is sulphide of iron alone that has the property of giving the test, and consequently its presence in the residue is confirmed.

#### § 14. ELEMENTS.

**92. The elements.** — By means of combination (synthesis) and decomposition (analysis) we have been able to distinguish between simple and compound substances. It is conceivable, however, that a substance which can unite with another to form a compound may itself be composed of other substances, so that under the proper conditions it may itself be decomposed. In such a case the substance is a component of the compounds formed from it, and it is a compound of the more simple substances which are to be regarded as its own components.

This may be represented by symbols. Assume that two simple substances A and B unite to form a compound AB. This substance AB can, on its part, unite with another substance C to form the compound ABC. Then AB is a *component* of ABC, or a *compound* in respect to A and B.

This is not merely an imaginary case, but it is one that is frequently encountered in practice. Water and the white residue obtained in the experiment on page 102 are two such substances; each of them can be decomposed into simpler substances by the union of which they may be formed again. One is never certain, therefore, on decomposing a compound into components,

that these latter may not themselves be susceptible to further decomposition.

For more than a century chemists have been attempting to make and decompose all the pure substances with which they have come in contact. They have attempted in every way imaginable to break down each substance into its simplest components, and the result of all these many-sided experiments may be expressed very briefly as follows.

There are at present about eighty substances that are known only as components and not as compounds. All other substances that have been studied have proved to consist of two or more of these eighty substances. All the means at our disposal have proved these last to be simple substances. They are called *elements*, and it may be asserted that all substances, and therefore all weighable bodies existing in nature, consist of one or more of these eighty elements, whether in the form of pure substances, solutions, or mixtures.

The majority of the substances with which we have experimented up to this point have been elements. This is true of sulphur, of mercury, of iron, and of iodine. On the other hand, water, hydrochloric acid, and alcohol are not elements but are compounds resulting from the combination of elements. Again, the sulphide of iron and the sulphide of mercury are compounds of the elements designated in their names.

**93. Chemical symbols.** — All compounds, therefore, may be characterized, as we have seen, by designating the elements from which they are formed or of which they consist. Chemists have, for convenience, invented a method for designating these elements that is independent of our everyday speech. The designations, or symbols, are practically the same throughout the civilized world and are used for designating chemical elements and compounds in textbooks written in Japanese, Turkish, French, German, English, etc. The system is International in about the same way as is the use of Arabic numerals and of musical characters.

Below are given the names of twenty-five of the best-known elements together with their symbols. Although most of these elements are well known only to scientists, quite a number of

them, especially the metals, are common substances and were known even to the ancients.

The symbols, as already indicated, are derived from the Latin or Greek names of the elements. Originally only the first letter was used for the symbol, but inasmuch as more elements were discovered in the course of time than there are letters in the alphabet, it is obvious that the names of several of the elements must begin with the same letter, so that in many cases it has become necessary to make use of a second letter, and the second letter chosen is not necessarily the one that comes next in the word, but it is the one that is as characteristic and prominent as possible in the name.

## A. NON-METALS.

Oxygen . . . . . O	Sulphur . . . . . S
Hydrogen . . . . . H	Nitrogen . . . . . N
Fluorine . . . . . F	Phosphorus . . . . . P
Chlorine . . . . . Cl	Carbon . . . . . C
Bromine . . . . . Br	Silicon . . . . . Si
Iodine . . . . . I	

## B. METALS.

Sodium . . . . . Na	Iron (Ferrum) . . . . . Fe
Potassium . . . . . K	Zinc . . . . . Zn
Magnesium . . . . . Mg	Manganese . . . . . Mn
Calcium . . . . . Ca	Lead (Plumbum) . . . . . Pb
Strontium . . . . . Sr	Copper (Cuprum) . . . . . Cu
Barium . . . . . Ba	Mercury (Hydrargyrum) Hg
Aluminium . . . . . Al	Silver (Argentum) . . . . . Ag

**94. Classification of the elements.** — In the above table less than one-third of the known elements are mentioned. Most of the other elements are not so well known because they occur less frequently and in much smaller quantities in nature, so that many of them were not discovered until quite recently. On the other hand, the elements are in many cases so closely related to one another, and behave so similarly with regard to combination with other elements, that it is possible to become acquainted with the most important types of chemical reactions

by the study of a few of the more representative or typical elements.

As a glance at the table shows, the elements may be divided into two large groups, *non-metals* and *metals*. Most of the elements of the first group are widely distributed in nature, and their chemical properties determine to a large degree the character of the chemical processes that take place on the surface of the earth, as well as in plants and in animals. Among these elements are found gases, such as oxygen, nitrogen, hydrogen, and chlorine, and on the other hand there are solids, some of which are readily fusible, as phosphorus and sulphur, and some of which are very hard indeed to melt, as carbon and silicon. Further, there is one liquid among them, namely bromine. These elements do not have metallic luster, do not conduct electricity well if at all, and since they have no other property in common than that of *not being metals* they are called the non-metals. Of the rarer elements which are not mentioned in the above table, only a few belong to this group; most of them are metals.

Among the metals are some that have been discovered during the last century, some only recently, and others which have been known since the days of antiquity. The former comprise, for the most part, the so-called *light metals*, some of which are lighter than water and in no case is the density greater than 3. The others are called *heavy metals*, for their density varies from 7 upward.

The light metals may be divided into three groups. Sodium and potassium belong to the *alkali metals*. The name alkali is derived from the Arabic and signifies soda and potash, which are compounds of sodium and potassium; besides these there are three other alkali metals of rare occurrence. Magnesium and calcium, as well as barium and strontium, belong to the *alkaline earth metals*, and aluminium to the *earths*. This last name arises from the fact that most rocks are compounds of aluminium, and their weathering products go to make up the surface of the earth. The name *alkaline earth* is given because the properties of this group of metals are intermediate between those of the *earths* and

those of the alkalis. To all of these groups belong quite a number of rarer elements which need not concern us.

It has for a long time been customary to classify the heavy metals into *base* and *noble* metals; to the former group belong iron, zinc, lead, copper, and to the latter mercury, silver, and gold. The difference between the two classes lies in the fact that exposure to the atmosphere affects the former but not the latter. The cause of this action is a chemical one; the metal combines with the oxygen and other constituents of the air. The base metals enter into such combination even at ordinary temperatures, especially in moist air. The noble metals, on the other hand, have so little tendency to combine with oxygen that they may be kept unchanged in the air, and if by other means they are made to combine with oxygen, the compound is decomposed by the action of heat and the original metal is obtained again. Advantage is taken of this property in the case of mercury for preparing pure oxygen from the air (p. 98).

**95. Conservation of the elements.** — The fact that the compounds are properly designated by the symbols of the elements from which they are formed, or into which they are decomposed, suggests an important natural law, which, however, must be explained more fully in order that it may be thoroughly understood. This law is called the *conservation of the elements* and signifies that it is impossible to transform an element into any other element either directly or indirectly. The chemists of the Middle Ages, who did not recognize this law, attempted over and over again to convert lead, iron, or other cheap metal into gold, but the experiments were always in vain. On the other hand, it is true that these many experiments of the alchemists have led to the law of the conservation of the elements, for it, like all other natural laws, is merely a result of experience and could only be formulated from an extensive knowledge of the chemical transformations which are actually possible.

In accordance with this law, whenever a compound substance is decomposed into its elements, the same elements are obtained in exactly the same proportions, irrespective of the way in which the decomposition is effected. For if from a certain com-

pound the elements A, B, and C were obtained by one method of analysis and in another way the elements A, B, and D, then this would be equivalent to a transformation of C into D. It would only be necessary to prepare the compound from the elements A, B, and C and then by the second method of decomposition decompose it into A, B, and D, to cause C to disappear and D to appear in its place. Such a transformation is contrary to the law and has never been effected.

Not only the *nature* of the elements but also the *weight relations* in a given compound are established by this law, independent of the way in which the compound is formed or decomposed. If, for example, it were possible by the decomposition of a compound AB to obtain different relative weights of A and B in one way than are obtained by another method of decomposition, then this again would be equivalent to a transformation of a part of A into B, or the reverse. The law is fulfilled only when the ratio is the same independent of the manner of synthesis or of analysis; and since the law has been found to be a general one, the reverse conclusion may be drawn that the elementary composition of a substance is independent of the manner in which it is formed or decomposed.

In all the most varied and complicated compounds formed under the influence of life in animal and vegetable substances, there has never been found any contradiction to this general law. We are inclined to regard the growth of a plant as such a wonderful process that the ordinary laws of inorganic nature do not come into consideration. Now it is true that there are many points in regard to the processes involved in animal and vegetable growth that we are not yet able to comprehend; still, on the other hand, the most carefully carried out experiments have shown that all the elements out of which the plant is composed come to it from without. These elements experience the most varied types of combination, but there has never been found in any plant an element that did not reach it from the outside.

## CHAPTER V.

### OXYGEN AND HYDROGEN.

#### § 15. OXYGEN.

96. **In general.**— In the experiment of heating the oxide of mercury (p. 98) a substance was obtained which was found to be a colorless gas and to have the property of causing a glowing splinter to burst into flame. This substance was called oxygen, and a glance at the table on page 108 shows that it is an element. Indeed, oxygen may be regarded as the most important element. It is likewise the most common element and comprises about one-half in weight of the surface of the earth as far as it is known to us. A part is present in the free state, as gaseous oxygen, but the greater part of it is present in a combined state, *i.e.*, as a constituent of oxygen compounds.

Free oxygen forms a part of the atmosphere in which we live. The air is a fairly complicated mixture of various gases one of which, water vapor, has been studied already (p. 88). Similarly, the water of the ocean, that covers such a large portion of the earth's surface, is really a complicated solution. The atmosphere is an ocean of air and is a reservoir of all the gaseous substances that are formed at any place on the earth's surface, just as the ocean of water contains in solution all the solid substances with which the water in springs, brooks, and rivers (all of which eventually empty into the ocean) comes in contact.

The chief constituent of the air is another element called nitrogen, which we shall study later; it suffices here to remark that nitrogen is a very inert element and does not under ordinary conditions enter readily into chemical combination. For the present, therefore, we may disregard its presence in all the experiments with the oxygen of the air.



Oxygen comprises about one-fifth of the air by volume (more nearly 21 per cent), so that its partial pressure in the air (p. 88) is approximately one-fifth of the total pressure; the air, therefore, behaves as *diluted oxygen*. This is the reason why a splinter that is merely glowing when in the air will burst into flame on coming in contact with pure oxygen gas. The glowing is caused by the combination of the elements of wood (which is itself a mixture of complicated compounds) with oxygen, whereby there is considerable evolution of heat, and the heat causes the glowing. When the glowing splinter is placed in pure oxygen, then the combination with oxygen takes place much more quickly, and instead of the slow glowing there is the rapid burning.

**97. The phenomenon of burning.** — It may be inferred from what has just been said that the ordinary burning of coal, kerosene, and illuminating gas has to do with a combination between the elements in the fuel and the oxygen of the air. Such is, in fact, the case. It is evident that the burning can take place only in the presence of the oxygen in the air, for the flame will go out if access of air is prevented. On the other hand, this does not prove that only a part of the air is available for effecting the combustion; to prove this, it is necessary to work with a *limited supply* of air.

Place a candle upon the end of a bent wire, the other end of which is run through a cork that tightly fits a large bottle. Lower the lighted candle into the bottle and insert the stopper into the neck (Fig. 33). The candle soon begins to burn feebly, and eventually goes out entirely. If now the bottle is allowed to become cold, it will be evident on removing the stopper that there is a slight vacuum in the bottle but only a very slight one. If the candle is taken out and again lighted, it will burn just as well as before; it has itself experienced no change that will account for the extinction of the flame while in the bottle. If the candle is again lowered into the bottle, it will this time burn only for a short time. It burns a few seconds because a little air has entered the bottle, but

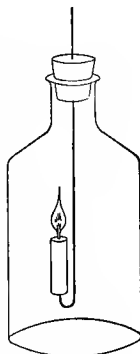


Fig. 33.

the candle goes out more quickly than in the first case when the bottle was filled with fresh air. It is evident, from this simple experiment, that combustible bodies will burn only for a limited time when in contact with a limited supply of air, and that the residual gas is incapable of supporting combustion.

The explanation lies in the law of constant proportions; the combustible substance of which the candle is composed combines in a certain definite proportion by weight with the oxygen of the air, and the quantity of the latter that is used up is, therefore, proportional to the quantity of the candle that is consumed. When there is no more oxygen available the burning must cease.

**98. Analysis of the air.** — The experiment with the candle does not suffice to show what proportion of oxygen is present in the air, because other gases are formed during the combustion of the candle. Phosphorus, on the other hand, is an element that forms a solid substance by union with oxygen. It has, furthermore, the property of burning spontaneously, even at the ordinary temperature, although slowly. With its help it is possible to make an analysis of the air.

On account of the fact that phosphorus in the air burns slowly

of itself, it is customary to keep this element under water. Place a piece of phosphorus about the size of a pea in a test tube, cover it with a little water, and heat gently. The phosphorus soon melts to a yellow liquid. Insert a long wire, bent somewhat at the end, into the liquid phosphorus and cause the latter to solidify about the wire, by placing the test tube in cold water. Place another test tube filled with air over a dish of water and introduce the phosphorus on the wire so that it is in the upper part of the tube (Fig. 34). Very soon a cloud of vapor, which consists of oxidation products of phosphorus, begins to form around

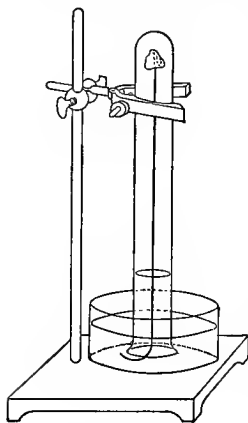


Fig. 34.

the phosphorus and sinks downward in the tube. The air begins to diminish in volume, as is shown by the fact that water

rises in the tube. This process continues for an hour or so, until finally all the oxygen in the tube has combined with phosphorus. From the quantity of water that has risen in the tube it is evident that the quantity of air in the tube has been diminished by at least one-fifth of its original volume, and this confirms the statement made on page 113. The residual gas at once extinguishes the flame of any burning substance.

**99. Pure oxygen.** — There are two ways in which pure oxygen may be prepared so that its properties may be studied: it may be separated from the air, or obtained by the decomposition of a suitable oxygen compound, care being taken in both cases to prevent contamination with any other gas. It is not altogether easy to separate pure oxygen from the air; it was only comparatively recently, after it was discovered how to obtain temperatures low enough to liquefy air, that it was found possible to carry out the process on a technical scale. If liquid air is available, it is only necessary to keep it for a short time in an open vessel. The nitrogen that is also present in the liquid air has a lower boiling point than oxygen and evaporates first, just as alcohol escapes first on boiling a mixture of alcohol and water (page 77). The liquid oxygen prepared in this way is a bluish liquid with a boiling point of  $-183^{\circ}$  C. If a glowing splinter is dipped in the liquid, it will burn with a brilliant flame in spite of the extremely low temperature.

The liquefaction and distillation of air are at present carried out regularly in large factories for the purpose of obtaining pure oxygen from the air. The oxygen is subsequently introduced into steel cylinders, under a pressure of 100 atmospheres, and thus handled commercially (Fig. 35). It is used for various purposes.

**100. Oxygen from potassium chlorate.** — For the laboratory, oxygen is either purchased in steel cylinders or else prepared from an oxygen compound. We have already seen that the oxide of mercury is a compound which is

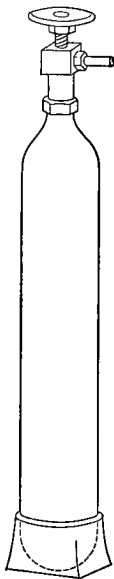


Fig. 35.

decomposed readily by heat into its constituents. This requires, however, a fairly high temperature, and inasmuch as only 8 g. of oxygen are combined with 100 g. of mercury, it is evident that the yield is not large. It is far more convenient to take a white substance known as potassium chlorate (or chlorate of potash); this salt is used in medical practice as a remedy for sore throat.

The substance consists of the elements potassium, chlorine, and oxygen, and on being heated it experiences a change whereby the potassium and the chlorine remain together and form a new solid substance, while the oxygen escapes as a gas and can be collected pure. The process is, therefore, perfectly comparable to the decomposition of oxide of mercury by heat, except that in this case a compound of potassium and chlorine rather than mercury remains behind, and nearly five times as much gas is obtained from the same weight of the original material.

First of all, experiment with a small quantity of the substance and heat it in a test tube. The small, white crystals melt readily to a colorless liquid which is liquid potassium chlorate; if the melt is allowed to cool at this point, the original solid will be obtained again. It is not until the temperature is raised above the melting point that bubbles of gas begin to be evolved, increasing in amount as the temperature is raised. If a glowing splinter is held at the mouth of the test tube, it will take fire, thus showing the presence of oxygen.

Now take away the test tube from the flame and add a little powdered pyrolusite. Although the liquid in the test tube has cooled somewhat, effervescence results just as on shaking sugar into a glass of plain soda water. The evolution of oxygen becomes very vigorous, so that sometimes the mass itself begins to glow; finally a black residue is left behind, which will be found to melt much more difficultly than the original potassium chlorate. The potassium salt in the residue dissolves readily in water, and on filtering the solution, unchanged pyrolusite remains, which may be dried and used over and over again for repeating the above experiment. On allowing the filtrate to stand for a

few days in a beaker covered with filter paper to keep out the dust, a white mass will gradually settle out which is similar in appearance to common salt and is altogether different from potassium chlorate. It is the above-mentioned compound of potassium and chlorine, called potassium chloride.

**101. Catalytic acceleration.**—A few words may be said concerning the action of the pyrolusite in the preceding experiment. The latter is a compound of oxygen with the element manganese, a metal similar to iron. The name pyrolusite was given to it before its chemical composition was known. It occurs quite commonly in mines and is used to discharge the brown or green tints of glass, or to color brown glazes and earthenware. Chemically, the substance is called manganese dioxide, or manganese peroxide. We shall subsequently study this substance more in detail. Here this is unnecessary because it takes no part chemically in this remarkable reaction, for it is found at the end of the experiment in precisely the same condition as at the start. It merely accelerates the evolution of oxygen from the potassium chlorate. Such cases where a slow reaction is accelerated by the presence of another substance, itself apparently unchanged during the reaction, are very numerous in chemistry; the acceleration is called *catalytic*, and the substance causing the acceleration is a *catalyzer*.

**102. Preparation of oxygen.**—Advantage is taken of the catalytic effect of manganese dioxide when it is desired to prepare a somewhat larger quantity of oxygen from potassium chlorate. The chlorate is mixed with about one-tenth its weight of manganese dioxide. The actual amount of the latter makes very little difference, because it is unchanged in the reaction, and it is not necessary to rub the two substances up together. The mixture is shaken into a flask which is provided with a fairly wide outlet tube, and this tube is connected by rubber tubing to another tube dipping into a vessel of water, so that the mouth of an inverted bottle filled with water can be placed over it (Fig. 36). The flask is heated cautiously, and soon bubbles of gas begin to escape. The first bubbles are not collected, because they consist merely of the air that was present

in the flask; it is only after the oxygen begins to be evolved rapidly that the escaping bubbles are collected. If the evolution of gas becomes too violent, the flame is taken away because the mass heats itself by its own decomposition and is therefore easily overheated.

From every gram of potassium chlorate about 200 cc. of oxygen gas are obtained. From this it is easy to calculate how much of the chlorate will be required, for example, to fill a five-liter bottle with gas. In carrying out the experiment it is best to take a little more than this quantity, because it is necessary to allow for slight losses such as at the beginning of the experiment when the air is being expelled from the flask.

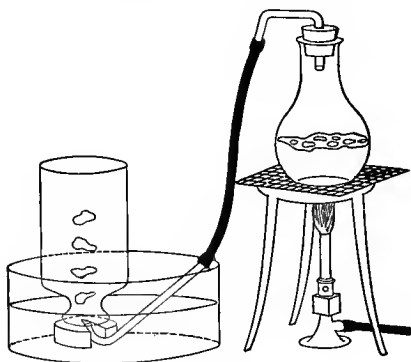


Fig. 36.

**103. Density of oxygen.** — A similar experiment can be used for computing the density of oxygen. It is necessary to determine the volume occupied by a given weight of the substance (*cf.* p. 13). The weight of oxygen is known if a weighed amount of potassium chlorate is used and the residue is weighed after the end of the reaction; according to the law of the conservation of weight, the weight of oxygen evolved must be equal to the loss in weight which the substance has experienced. The space occupied by the gas can be estimated by a very simple gasometer which we make in the following way. Take a bottle somewhat taller than it is wide, of about one liter capacity, and provide it with a

two-holed stopper. Through one hole pass a short, right-angled tube and join it to rubber tubing so that it can be connected with the gas generator. Through the other hole in the stopper insert another tube that reaches to the bottom of the bottle and is connected above with rubber tubing carrying a pinch cock, and with an outlet tube. The bottle and tubing are completely filled with water.

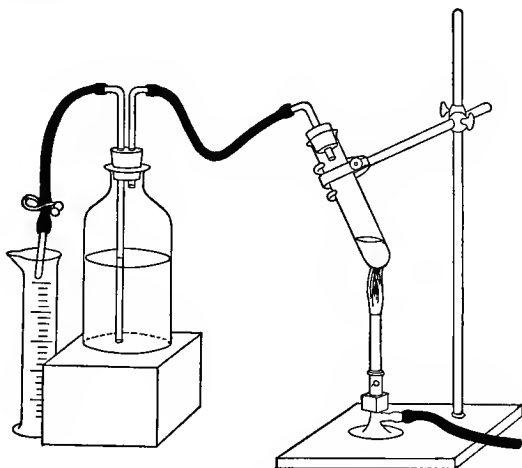


Fig. 37.

Choose a thick-walled test tube to hold the potassium chlorate, and weigh the tube empty and then with about a gram of potassium chlorate in it; the difference between the two weights gives the exact amount of potassium chlorate used in the experiment. Close the test tube with a well-fitting stopper that carries a glass tube connecting with the rubber tubing of the gasometer. Have the outlet tube from the bottle leading to a graduated cylinder by means of which the quantity of water that runs off during the experiment can be measured.

Now heat the bottom of the test tube and open the pinch cock; oxygen is soon evolved and drives out the water from the bottle into the graduated cylinder. Continue the heating as long as gas is being evolved. Then remove the flame, close the pinch-cock, and allow everything to cool. Finally place the end of the

short tube under the surface of the water in the graduated cylinder, open the pinch-cock, and by raising or lowering the cylinder, bring the level of the water in it to the same height as that of the water in the bottle. Then the quantity of water that has flowed from the bottle is exactly equal to the volume of gas that it contains, and this volume is determined by means of the graduated cylinder.

Weigh the test tube with the solid remaining in it; the loss in weight represents the weight of oxygen in the bottle. Thus the two values required for the determination of the density are known.

If, for example, the loss in weight is found to be 0.382 g. and the volume 286 cc., the density of the oxygen is  $\frac{0.382}{286} = 0.00137$ .

It is a well-known physical principle, however, that the volume of a gas varies with the pressure and the temperature, so that different values will be obtained for the density of oxygen under different conditions of temperature and atmospheric pressure. It is customary, therefore, in scientific measurements of gas density to compute what it would be at 0° C. and 76 cm. of mercury pressure. From the observed volume of the gas the volume at 0° and 76 cm. pressure is computed in accordance with the gas laws.

As regards the influence of temperature, it is known that the space occupied by a gas at  $t^\circ$  C. compared to the volume which it would occupy at 0° C. is as  $273 + t$  is to 273. In other words, the observed volume must be multiplied by the fraction  $\frac{273}{273 + t}$  in order to determine what the volume would be at 0° and the same pressure. It is also known that the volume of any gas is inversely proportional to the pressure. If, therefore,  $b$  is the barometric pressure measured in centimeters of mercury, the observed volume should be multiplied by  $\frac{b}{76}$ , in order to find what the volume of the gas would be at 76 cm. pressure. If now  $V$  represents the observed volume, then  $V \cdot \frac{b \cdot 273}{76(273 + t)} = V_0$ , the "reduced" volume. The exact density of oxygen under



these *standard conditions* is 0.001429. In the above experiment certain sources of error were disregarded, so that the values actually obtained will vary somewhat from the truth.

**104. Properties of oxygen.** — Oxygen is colorless and odorless. This is obvious from the fact that air itself has these properties and oxygen is present in the air in an uncombined state. Oxygen is only very slightly soluble in water, so that it can be collected over water, as in the above experiments, without appreciable loss of gas.

In chemical respects, oxygen gas is characterized by the fact that it is capable of entering into chemical combination with many substances that occur in nature. At ordinary temperatures, to be sure, this is hardly true, although the reactions take place readily when the substances are heated. A large number of substances from which utensils, houses, clothes, books, etc., are made are capable of combining with oxygen, or burning, and yet we attach considerable value to these substances. If oxygen, on account of the presence of some catalyzer (p. 117), should suddenly acquire the ability to combine with these substances at ordinary temperatures, then all our culture would vanish, for not only would our wooden houses burn up, but our clothes, libraries, valuable papers, and even our own bodies would all be consumed, for all these substances can be made to take fire and burn.

That combustion is merely a combination of the burning substance with oxygen has already been shown. Since only one-fifth of the air is oxygen, combustions take place much more rapidly in pure oxygen and the resulting temperature is much higher. When the oxygen of the air is used for a combustion, the resulting heat is partly used up in raising the temperature of the atmospheric nitrogen, and this itself takes no part in the process. In pure oxygen there is no such waste of heat, and this explains why a higher temperature is obtained. The phenomena attendant upon combustion in pure oxygen are, therefore, somewhat different from those occurring in air. For performing the following experiments use liter bottles filled with the gas as described in the experiment on page 118.

The fact that wood which is only feebly glowing will burst into flame and burn with uncommon brilliancy when placed in contact with pure oxygen, has already been shown repeatedly. A piece of coal, fastened to a wire and introduced, while faintly glowing, into a bottle of oxygen, will glow brightly. Sulphur placed in an iron deflagrating spoon and ignited in the air burns with a flame so pale that it is scarcely visible in daylight. In oxygen the flame becomes larger and is a more brilliant blue. Phosphorus burns in the air with a yellow flame not much different from that of a stearin candle; when introduced into a jar of oxygen gas, it burns so brilliantly that it blinds the eye after a short time. This last experiment is not an altogether safe one for the beginner to attempt.

Perhaps the most remarkable phenomenon is the burning of iron in oxygen. For this experiment it is best to use the main-spring of a watch, which has been softened by heating in the air and coiled up into a loose spiral. Fasten a piece of slow match to one end of the wire (or dip it in melted sulphur), light this and lower it while glowing into a jar of oxygen. The tinder at first burns, causing the end of the iron to become so hot that it also begins to burn. The combustion continues with a brilliant display of sparks, and meanwhile the product of the combustion of iron and oxygen drops to the bottom of the jar in the form of glowing, melted globules; the glass usually breaks unless the precaution was taken of sprinkling sand upon the bottom of the jar so that the hot particles do not come into immediate contact with it.

This last experiment illustrates a principle which is of considerable technical importance, since it is possible to cut iron, even when in the form of thick plates, by the aid of an oxygen blast. At the place where it is desired to cut the metal, it is heated with a blast flame of illuminating gas and with an excess of oxygen. When the iron begins to burn the supply of oxygen is increased. The blast is regulated by means of a mechanical device so that it is possible to make the cut with great sharpness and precision.

In all these cases the burning substance unites with oxygen to form a compound. With carbon and sulphur the compounds

formed are gases, so that it is not possible to see them. With phosphorus a white snow-like substance results, which dissolves readily in water; with iron a grayish-black solid is obtained.

**105. Acids.** — If the blue solution of a dyestuff called litmus is placed in the bottles in which carbon, sulphur, and phosphorus were burned, the solution will turn a violet red in the first case and a yellowish red in the others. There exists a large class of substances, called *acids*, that have this characteristic property of turning blue litmus red. It is evident, then, that acids sometimes result from the combination of an element with oxygen. In fact it was formerly thought that all acids were compounds containing oxygen, and the name oxygen is derived from Greek words that mean *acid* and *to produce*. If, however, litmus solution is placed in the jar in which the iron was burned, there will not be any red coloration; as a matter of fact, the compound formed in this case is not an acid but belongs to a quite different class of substances. To-day the name oxygen is retained merely to designate the element without regard to its original significance.

**106. Heat of combustion.** — The remarkable luminescence produced by the combination of oxygen with other elements indicates that large quantities of heat are set free. In this respect the process is similar to the liquefaction of a vapor, or to the solidification of a liquid, but the quantities of heat liberated during chemical changes are, as a rule, much greater than those attendant upon a change in state.

Of all chemical changes, the combinations with oxygen are the most important. Almost all the mechanical work that is performed in such extraordinary amounts in the various technical fields (railroads, factories, electric power houses, etc.) is obtained from the heat that is set free as a result of the chemical combination of a combustible fuel with oxygen, or, in other words, from the *heat of combustion*. The heat is utilized, in the first place, to convert water into steam, and the latter performs work in the steam engine. Ordinarily coal alone is regarded as the food upon which commerce is nourished, because coal is necessary for combustion and must be paid for, whereas oxygen is

obtainable without cost in practically unlimited quantities. Oxygen, however, is just as indispensable for the purpose of obtaining heat of combustion as is the fuel itself; if it were possible to limit the supply of oxygen then it would be sold like coal.

Oxygen, however, is not only indispensable for industrial purposes, but man and animals cannot exist without it. Not only the heat of the living body, but all kinds of work performed by it, including mental as well as bodily activity, are at the cost of the combustion of certain substances. Life itself requires an abundant supply of oxygen, and when this fails suffocation results. The combustible substances are the foods, and it is the reciprocal action between these and oxygen that is the source of heat and work. The fact that the combustion of food in the animal body takes place without flame does not signify that there is any essential difference between this process and that of the combustion of foods in a stove; in the analysis of air by means of phosphorus (page 114) the latter burned in the cold without flame, and consequently the combustion took place much more slowly than if the phosphorus had taken fire (page 122). In exactly the same way the food may burn rapidly with flame, or very slowly without it. The quantity of heat set free during the combustion is exactly the same in both cases, although in the first case it is set free in a short time and thereby the temperature of the combustion products is raised very high, whereas in the other case so much time is required that the heat is dissipated and there is only a slight rise in temperature.

The fact that the quantities of heat liberated must be the same in both cases, provided the end products are the same, can be demonstrated in a manner quite similar to that described on page 42. In that case we saw that the reversal of any process by which heat was evolved, or absorbed, must result conversely in the consumption or evolution of exactly the same quantity of heat, as otherwise a method would be obtained of either creating a certain amount of heat from nothing or of causing it to disappear into nothing; experience has shown that this is never possible. Similarly it can be asserted that in the reversal of a chemical reaction there must be at the same time a reversal of

the heat effect. Since the same chemical process may be made to take place at one time quickly and at another time very slowly, and the process may be reversed each time in the same way, the conclusion must be drawn that equal amounts of heat are liberated in each of the original cases, for their action can be prevented in each case by the same reversed process. If the quantity of heat set free by the rapid combustion is designated as  $A_1$ , that of the slow combustion as  $A_2$ , and that of the opposite action as  $B$ , then  $A_1 = -B$ , and  $A_2 = -B$ , so that obviously  $A_1 = A_2$ .

**107. Names of oxygen compounds.** — The compounds of oxygen with other elements are called *oxides*. Oftentimes it happens that an element forms two oxides; the one with the smaller proportion of oxygen is designated by adding the syllable *ous* to the name of the other element (*e.g.*, ferrous oxide, manganous oxide) and the syllable *ic* to designate the oxide with the larger proportion of oxygen (as ferric oxide, manganic oxide, etc.). An oxide with relatively less oxygen is sometimes called a suboxide, and one with the most oxygen is often termed a peroxide. Another method of nomenclature is to designate the relative amounts of oxygen by mean of Greek numerals, as monoxide, dioxide, trioxide, tetroxide, pentoxide, etc.

It was mentioned on page 123 that the compounds formed by the combination of non-metallic elements with oxygen were often called acids. Frequently oxygen combines with these elements also in more than one relation. Here again the same use is made of the suffixes *ous* and *ic* and of the prefix *per*, but instead of *sub* it is customary to use the prefix *hypo*, *e.g.*, hypochlorous acid, chlorous acid, chloric acid, and perchloric acid, the relative amount of oxygen present in the compound increasing in the order named.

**108. Theory of combustion.** — The phenomena of combustion belong to the most striking and most frequent of chemical processes and consequently have always attracted the attention of chemists. Since the combustion process is so frequently observed in connection with the burning of wood, coal, wax, tallow, etc., the impression is gained that by the process a substance is

annihilated, or at least largely diminished in bulk, and that during the combustion something is lost. At the present day we know that gaseous substances are formed which are invisible and pass away from the vicinity of the burning body, but as a matter of fact the weight of the products of combustion is greater than that of the original substance, and the gain in weight represents the quantity of oxygen that has entered into combination. This fact can be made very clear by means of a simple experiment in which the escape of the gaseous products of combustion is

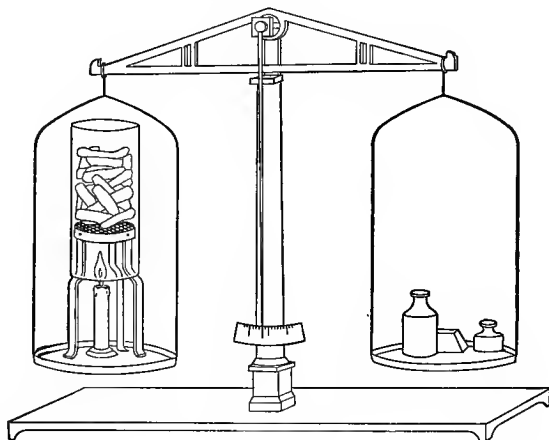


Fig. 38.

prevented. Caustic soda, a substance that can be purchased in the form of white sticks, can be used to catch these products. Place a small candle in one pan of a balance and over it support a lamp chimney which is loosely filled with sticks of caustic soda resting upon a wire gauze; place weights in the opposite pan until the balance is in equilibrium and then light the candle (Fig. 38). After a short time it will be noticed that the side of the balance at which the candle was placed becomes heavier, and a crust begins to form on the sticks of caustic soda. The gain in weight represents the oxygen of the air that has combined with the hydrogen and oxygen of which the candle is composed.

Chemists never made such experiments as this until toward the end of the eighteenth century, and before that time it was assumed that something escaped from substances which burned. This thing was called *phlogiston*. Consequently, the oxides were regarded as elements and our present-day elements were considered as compounds of the elements with phlogiston. This theory was perfectly satisfactory to distinguish between the taking up and giving off of oxygen, but its error became apparent as soon as pure oxygen was discovered and the part that it plays in combustion understood. Oxygen was discovered in 1770 by Scheele and in 1774 by Priestley; the proof that the theory of combustion had to be reversed in order to coincide with the actual changes in weight, and that instead of the hypothetical phlogiston it was, as a matter of fact, the detectable element oxygen that must be considered as the cause of combustion, remained to be shown by the French scientist, Lavoisier, in 1783. His work was carried out on the basis of the law of the conservation of weight, which, although he did not himself discover it, he showed for the first time to be of such great significance in the study of chemical processes.

**109. Combining weights.** — Of all the elements, oxygen enters into the most combinations with other elements; in fact fluorine is the only known element which it has been found impossible, up to the present time, to make combine with oxygen. Consequently, it is possible to give for every other element a relative number that represents the quantity which will combine with a given quantity of oxygen. It would have been simplest to compute all these values to a unit weight of oxygen, but as a result of a complicated historical development it has become customary to refer these values to 16 parts by weight of oxygen. These numbers are called the *combining weights* of the elements and they represent the relative amounts by weight which combine with 16 parts of oxygen to form chemical compounds.

Certain elements, however, combine with oxygen in more than one relation, so that different combining weights could be assigned to the same element. This, however, leads us to another important general law called the *law of multiple proportions*, which

may be enunciated as follows: *when an element combines with oxygen in more than one relation, then the weights of the element that are combined with the same weight of oxygen bear a simple, rational relation to one another.*

Thus we have found that mercury combines with oxygen in the relation of 100 : 8 (p. 116). This gives 200 parts of mercury as equivalent to 16 parts of oxygen. Another oxide of mercury is known, however, which instead of being red is black, and this black oxide contains 400 parts of mercury, or twice as much, to 16 parts of oxygen.

Obviously, according to the above definition, two different combining weights can be assigned to mercury, namely 200 and 400. On the basis of the law of multiple proportions, however, it is considered better to assign to mercury the combining weight of 200 and assume that there are two combining weights of mercury to one combining weight of oxygen in the black compound. Of course we might also say that one combining weight of oxygen is combined with half a combining weight of mercury in the black oxide, but it has become customary never to use fractions of a combining weight, and for this reason the first statement is the only one that is permissible.

The law of multiple proportions is by no means limited to oxygen compounds, but it holds equally true for the compounds of any elements with another element. Every time an element is found to combine with another element in more than one relation, the amounts of the one element referred to a given weight of the other are always in simple rational ratios. These ratios are not necessarily, as in the case of mercury, the simplest possible, namely 1:2, but they may be 1:3, 2:3, 1:4, 3:4, 1:5, etc.

The combining weights, according to the definition given above, are referred to the compounds of the different elements with oxygen. Evidently it would be possible to determine, in the same way, for every element a series of combining weights, showing how much of the other elements will combine with a given amount of the element in question. This, however, is unnecessary, for it has been found to be a perfectly general



law that *the combining weights in the oxygen table also represent the amounts of the other elements which combine with one another.*

Since, however, in these last compounds several relations are often found, the law of multiple proportions also comes into consideration. We may summarize, then, as follows:

*The elements combine with one another only in the relations of their combining weights or in multiples of the same.*

Thus, for example, the combining weight of mercury is 200, as we have just seen, whereas the combining weight of sulphur must be placed at 32, because  $2 \times 16$  and  $3 \times 16$  parts of oxygen have been found to combine with 32 parts by weight of sulphur in the oxides of sulphur. If it is desired to know the ratio in which mercury and sulphur combine, the simplest possible one, where one combining weight of each element is present, will be 200:32. Now  $200:32 = 6.25:1$ , and this last ratio was found by direct experiment (p. 95) to represent the relations by weight in which these two elements combine with each other.

**110. The atomic theory.** — Somewhat more than one hundred years ago the English chemist, John Dalton, suggested a conception concerning the composition of matter which depicts very clearly the actual relations and therefore serves as an excellent aid for teaching and for investigation. This conception is the *atomic theory*.

Even the old Grecian philosophers had the idea that all substances were composed of smallest particles, and that these particles were so small that they were not visible and could not be divided further without the substance losing its nature. Hence these were called *atoms*, meaning indivisible. During the development of science, up to the beginning of the modern period, this idea was very generally held, but without much influence in the study of natural phenomena, and it remained for Dalton to make it fruitful.

The question arises whether one must assume that all the atoms of a given element are similar but of somewhat different sizes, such as perhaps grains of sand, or whether it must be assumed that they are all perfectly identical with one another.

The last assumption has been found to be more probable and for the following reasons.

If the atoms of an element like bromine<sup>1</sup> were not all alike, then it would be expected that by a partial distillation, or by a partial freezing, it would be possible to separate bromine into a portion that boils or freezes a little lower than the remaining portion, for the properties would naturally depend somewhat upon the size of the atoms. Since, however, a pure substance is characterized, as we have seen, by the fact that it is transformed under *constant* conditions into another state, it must be concluded that the element is composed of atoms that are perfectly identical with one another. The atoms of different elements must be different as regards size and shape, as otherwise the properties would not be different. On the other hand, the atoms of any given element must also have the same properties when placed under the same conditions, irrespective of where the atoms are found or how they are prepared, for the properties of pure substances have been found independent of such circumstances.

Moreover, it follows from the law of the conservation of the elements that a given atom cannot be transformed into an atom of any other element; if this were possible one element could be made from another and a given element could be made to disappear entirely. The process of chemical combination must be regarded as the union of atoms of different elements with one another; in this way compounds are formed. For this reason the atoms can be obtained again from the compounds. In elements all the atoms are alike, whereas in compounds the atoms of different elements are present. Compounds, however, are also composed of smallest particles, which, by the same reasoning as applied above to bromine, are all perfectly similar to one another, and these particles cannot be divided without the compound losing its identity. To avoid confusion, another name (molecules) is now given to these smallest particles of a compound (*cf.* p. 288), although in the original sense the term *atom* was applied to all substances.

<sup>1</sup> Bromine is chosen for illustration simply because it is liquid at ordinary temperature.

This method of representation corresponds perfectly to the stoichiometrical laws, *i.e.*, to the laws governing the weight relations of the elements and compounds. If all the atoms of a given element are alike, then each one will have the same weight. The exact size of an atom is unknown; we merely know that all the atoms of oxygen, for example, have the same weight wherever the atom may be found. The same is true of the atoms of every other element, *e.g.*, mercury. If, therefore, a compound, oxide of mercury, is formed from oxygen and mercury then an atom of mercury unites with an atom of oxygen, and since each individual atom has its own definite weight, then the relations by weight in which the elements combine with one another must be equal to the weight relations of the individual atoms. For, irrespective of the actual number of oxygen and mercury atoms present in one gram of oxide of mercury, we know that there are just as many atoms of mercury as there are atoms of oxygen, so that the relations by weight in which the elements are found to combine in an experiment (*cf.* p. 95) represent at the same time the weight relations of the individual atoms.

The combining weights, therefore, can be regarded as the relative weights of the atoms. They have, in fact, been given the name *atomic weights*. If one can imagine a balance constructed so delicately that an individual atom could be weighed upon it, then 16 atoms of hydrogen would weigh as much as one atom of oxygen; or, in order to counterbalance an atom of mercury, we should have to place in the opposite pan 12 atoms of oxygen and 8 atoms of hydrogen.

The atomic theory, therefore, serves to explain the laws of constant proportions and of combining weights. We next come to the law of multiple proportions. If the element A combines in several relations with the element B, then in the sense of the atomic theory, this can take place only by a combination of different numbers of atoms of the two elements. In one compound there may be present one atom of A and one atom of B, in another two atoms of A and three atoms of B, in still another the atoms may be in the ratio of 1 : 2 or in any other simple

ratio that is expressed by whole numbers. In accordance with this, the weights of the elements in these different compounds must bear a simple relation to one another, which is represented by whole numbers, for since the atoms are indivisible there must be present in each compound a whole number of atoms. This is merely another way of expressing the law of multiple proportions.

It is evident, then, that the weight relations of chemical compounds can be perfectly and clearly expressed by the supposition of the existence of atoms. This makes it seem very probable that substances are actually so constituted, and this view has been confirmed by discoveries in entirely different fields. Consequently we shall make repeated use of this theory in this book.

To be sure, a number of closely related questions remain to be answered. The most important of these is with regard to how the properties of a compound depend upon those of the constituents. In general, the properties of a compound are quite different from those of a mixture or of a solution prepared from the elements. Thus, for example, a mixture of sulphur and mercury has a yellowish-gray appearance, whereas the compound containing the same amounts of the elements is black, and, furthermore, the compound is a solid at temperatures where either of the constituents would be in the liquid state. It is, indeed, this fact that the properties of a compound are essentially different from those of the constituents, which is a characteristic of chemical reactions.

We must, therefore, draw the conclusion that the properties do not depend solely upon the nature of the constituents, or of the atoms, but upon certain other determinative conditions. We have seen that in the change of state of a pure substance there is either an evolution or an absorption of a considerable quantity of heat. In chemical reactions, in the narrow sense, the evolution of heat, or the change in energy, is usually much larger, and therefore it is to be expected that there will be a correspondingly greater change in properties.

**III. Table of combining weights.** — Inasmuch as the knowledge of the weight relations of all chemical compounds depends

upon a knowledge of combining weights, it is necessary to make constant use of these numbers in carrying out chemical investigations, in order to estimate how much of a given substance is to be taken for a reaction, how much of a product is to be expected, or how much of an element is present in a compound. Below is given a table showing the combining, or atomic, weights of some of the more important elements, and every one who is engaged in making chemical experiments does well to post such a table over his working bench.

## COMBINING WEIGHTS OF THE MOST IMPORTANT ELEMENTS.

Non-Metals.		Metals.	
Oxygen . . . . . O	16.00	Sodium . . . . . Na	23.00
Hydrogen . . . . . H	1.01	Potassium . . . . . K	39.10
Fluorine . . . . . F	19.0	Magnesium . . . . . Mg	24.32
Chlorine . . . . . Cl	35.46	Calcium . . . . . Ca	40.09
Bromine . . . . . Br	79.92	Strontium . . . . . Sr	87.63
Iodine . . . . . I	126.92	Barium . . . . . Ba	137.37
Sulphur . . . . . S	32.07	Aluminium . . . . . Al	27.1
Nitrogen . . . . . N	14.01	Zinc . . . . . Zn	65.37
Carbon . . . . . C	12.00	Iron . . . . . Fe	55.85
Phosphorus . . . . . P	31.04	Manganese . . . . . Mn	54.93
Silicon . . . . . Si	28.3	Lead . . . . . Pb	207.10
		Copper . . . . . Cu	63.57
		Mercury . . . . . Hg	200.0
		Silver . . . . . Ag	107.88
		Tin . . . . . Sn	119.0
		Gold . . . . . Au	197.2
		Platinum . . . . . Pt	195.2

## § 16. HYDROGEN.

112. **Water.** — Hydrogen, like oxygen, is a gaseous element, although, unlike the latter, it does not occur free in nature but only in the form of chemical compounds. Of these, the most important is *water*, which is composed of hydrogen and oxygen. In accordance with the law of constant proportions, it is desirable to know the ratio by weight of the two elements in the compound. This has been determined very accurately and found to be 1.008 : 8 or very nearly 1 : 8. Water, therefore, consists chiefly, as far as its weight is concerned, of oxygen.

That water is actually a compound substance cannot be shown as in the experiment with oxide of mercury, by simply heating the substance to a moderately high temperature, for steam does not begin to decompose into the elements until a temperature of  $1600^{\circ}$  is reached; at a somewhat lower temperature the elements recombine to form water. For this reason, it was a long time before the chemical composition of water was known, and even then it was not established by decomposing water but by synthesizing it. In other words, the element hydrogen was first discovered, and it was found that this produced water on being burned; from this it was reasoned that water contains hydrogen. Subsequently, however, a way was discovered for decomposing water into the elements.

Just as in the case of sulphide of mercury, which could not be decomposed by merely heating it, water can be decomposed by giving the oxygen in it a chance to combine with some other element. For this purpose zinc may be used.

Zinc, as a matter of fact, decomposes water even at ordinary temperatures, but the reaction takes place so slowly that it is not practicable to carry out an experiment in this way. If, however, the zinc is heated and steam comes in contact with it, then the decomposition takes place very easily. Place about a cubic centimeter of water in a test tube, shake over it a little commercial zinc dust and heat the upper part of the tube so that the zinc becomes hot before the water can evaporate. An evolution of gas soon takes place. Collect, in the usual manner, some of the gas over water in a small cylinder, after allowing the first portions of the gas to escape as they are contaminated with air.

The gas thus obtained does not, like oxygen, support combustion; but it takes fire in the air when it is brought in contact with a flame. Since a combustion usually signifies a union with oxygen, it is easy to understand that water is formed when hydrogen burns.

The following change has, therefore, taken place:

Zinc + Water gives Zinc oxide + Hydrogen;

*i.e.*, the oxygen that was formerly united with hydrogen has com-

bined with the zinc and gaseous hydrogen has been evolved. One of the chief characteristics of hydrogen is that it burns in the air with a pale blue flame.

113. **Other methods of preparation.** — In the laboratory, a more convenient process for preparing hydrogen is to decompose a hydrogen compound other than water in such a way that hydrogen is set free. The hydrogen compound most frequently used is contained in hydrochloric acid.

We have already met with this substance (p. 105) and found it to be a colorless liquid like water. It is not a pure substance but an aqueous solution of a compound called hydrogen chloride. Hydrogen chloride consists, as its name implies, of the elements hydrogen and chlorine and is a gas which is quite soluble in water. Chlorine is an element which, like oxygen, combines readily with metals. If, therefore, a suitable metal is placed in contact with hydrochloric acid, the chlorine combines with the metal and hydrogen is liberated. Iron, aluminium, zinc, etc., may be used as metal; but it is customary to employ zinc, although not necessarily in the form of dust as in the above experiment. The compound called zinc chloride, formed by the reaction, is very soluble in water and, therefore, remains dissolved in the colorless liquid.

A large number of different gas generators have been devised by means of which it is possible to prepare readily as much gas as is desired. One of the simplest of these is shown in Fig. 39. It consists of a bottle, of suitable size, in which the zinc is placed in the form of sticks, strips of sheet zinc, or granules obtained by pouring molten zinc into water. The bottle is closed with a two-holed stopper; in one hole is put a short right-angled tube through which the gas is to escape, and in the other hole a glass-stoppered funnel through which the hydrochloric acid enters

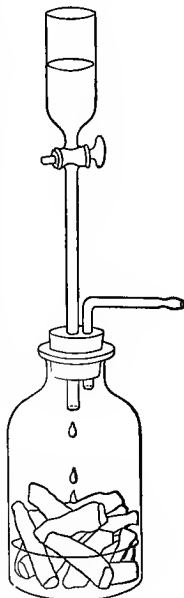


Fig. 39.

the bottle. By carefully opening the stopcock the acid flows into the bottle, drop by drop, and there is a correspondingly steady stream of hydrogen evolved, which ceases as soon as the stopcock is closed.

At first quite a considerable amount of acid is run in so that the air in the bottle is quickly expelled, after which the escaping gas is collected in a small inverted test tube filled with water (*cf.* Fig. 31, p. 99). When the tube is filled with gas, close it with the thumb and bring it close to a flame with the mouth of the tube upward. The first tube will probably contain only air, so that nothing especial will happen. Soon, however, a tubeful of gas will be obtained which will give a loud pop when brought in contact with a flame, and finally, when a tube filled with pure hydrogen gas is ignited, the gas will burn quietly. When the gas has been shown by such a test to be pure, it is ready to be used for further experiments.

**114. Detonating gas.**—Since the bottle used in the last experiment was originally filled with air, the gas that escapes from it is at first a mixture of hydrogen and air. This mixture of gases is dangerous to handle, because, like gunpowder in a confined space, it requires only a spark to make it explode. The explosion is due to the fact that the combustible substance, hydrogen, and the oxygen required for its combustion are mixed together so that when they start to combine with each other the whole combination takes place *suddenly* before it can be stopped. If a pure combustible gas is allowed to flow into the air and is lighted, as for example when illuminating gas is lighted in a dwelling, the mixing of the air with the combustible gas takes place only at the borders of the flame, and it is there that combustion takes place. The inner part of the flame is cold. If a platinum wire is held diagonally across a flame, the wire will be heated to glowing only where it touches the edges of the flame; the wire is just as dark inside the flame as it is on the outside of it. If, however, the gas is previously well mixed with air, then the combination is in no way limited but takes place instantaneously throughout the entire mixture and breaks glass vessels into small fragments,



just as gunpowder when ignited will burst the bomb in which it is confined. Herein lies the danger of mixtures of air and illuminating gas which result when the gas is allowed to stream into a room without being lighted at the burner. An explosion is likely to result if a match is lighted in such a room. Still more dangerous is *detonating gas*, a mixture of oxygen and hydrogen. To be sure, the small amounts present in a small test tube are not at all dangerous, for since the mouth of the tube is as wide as the remaining portions, the force of the explosion is exerted outward and hence merely a loud report results; in this case the walls of the tube are strong enough to bear what pressure is exerted against them.

**115. Properties of hydrogen.** — After the gas from the hydrogen generator has been found to be pure, by the fact that a sample of it will burn quietly, collect a few cylinders of the gas (*cf.* p. 118) so that its properties may be studied. The fact that it is not perceptibly soluble in water is evident because the size of the bubbles do not diminish as they rise through the liquid. It is also evident that the gas is colorless.

If a cylinder of the gas is allowed to stand uncovered a short time with its mouth up, it will then be found that the gas in the cylinder will not take fire; a burning taper can be lowered to the bottom of the cylinder and there will be no evidence of anything but air in the vessel. On the other hand, if the open cylinder is left supported in such a way that its mouth is down, the gas can be lighted even after the cylinder has been left open for several minutes. This proves that hydrogen gas, exactly contrary to the behavior of liquid water, flows upward but does not flow downward. This is because hydrogen is lighter than air and, therefore, it flows upward, just as air flows upward into water if a bottle is unstoppered under water with the mouth of the bottle uppermost; on the other hand, if the bottle is inverted, it may be opened under water without any of the air escaping.

In reality air is more than fourteen times as heavy as the same volume of hydrogen. A cubic meter of air, under the ordinary conditions of temperature and pressure, weighs about

1200 grams, whereas a cubic meter of hydrogen under the same conditions weighs only about 86 grams. At  $0^{\circ}$  and 76 cm. pressure one cubic meter of hydrogen weighs 89.8 grams.

This is the reason for the use of hydrogen gas for filling balloons and airships, the buoyancy of which can be estimated by the above figures; if the hydrogen is pure, one cubic meter of it will lift about 1 kg. It is evident, therefore, that a relatively large volume of the gas has to be used, for it is necessary in an airship not only to lift one or more persons but sometimes machinery as well as the whole envelope for the gas. For this and other purposes, hydrogen, like oxygen, is now being manufactured on an industrial scale and is compressed in steel cylinders sometimes under 100 atmospheres. Such a bomb of 100 liters capacity would contain  $100 \times 100$  liters of hydrogen or 10 cubic meters under ordinary atmospheric pressure.

Even the small toy balloons are filled with hydrogen. Such a plaything loses its buoyancy in a few days and becomes much smaller in size. This does not necessarily mean that there is a leak at the tied opening through which the balloon was filled, but the leakage is due to the property that hydrogen has of diffusing very rapidly, *i.e.*, it passes rapidly through pores which are so fine as to prevent wholly or partly the escape of most other gases.

**116. Diffusion.** — This particular property is influenced greatly by the very low density of hydrogen gas (hydrogen is the lightest of all known gases). It may be illustrated clearly by the following experiment. Provide a cell of porous clay, such as is used for galvanic elements, with a stopper, and through this insert a long, straight tube open at both ends; support this, as shown in Fig. 40, so that the lower end dips into a dish containing some water, and add some litmus to the latter to make it more plainly visible.

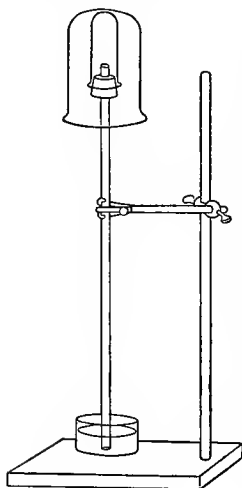


Fig. 40.

lower end dips into a dish containing some water, and add some litmus to the latter to make it more plainly visible.

Over the cell place a large inverted beaker. If now a rapid stream of hydrogen is led into the space between the beaker and the porous cell, it will soon be noticed that some bubbles of gas escape from the bottom of the tube. This is due to the fact that hydrogen passes through the cell wall faster than air can escape in the reverse direction, so that the latter seeks a chance to escape through the tube. After a short time a state of equilibrium is reached and no more bubbles of air pass through the water. Now take away the beaker from the top of the apparatus and notice that water ascends in the tube until it reaches quite a height and then begins to fall again. When the beaker is removed there is no longer an atmosphere of hydrogen surrounding the cell and, therefore, hydrogen flows outward and diffuses through the porous wall faster than air can get in to take its place; this causes a partial vacuum within, and consequently the water rises in the tube. Since, however, the cell is not air-tight, this vacuum will not hold, and soon air enough will enter the cell to equalize the pressure and the water column falls. This experiment, therefore, depends entirely upon the different rates of diffusion of hydrogen and air.

The fact that hydrogen, in spite of differences in the total pressure, seeks to reach those places where there is no hydrogen is due to a general property of all gases. Every gas constantly strives to distribute itself within other gases in precisely the same way as if no other gas were present; in other words, a state of equilibrium is not reached until the gas is uniformly distributed in all accessible directions. We met with a similar case (p. 88) when we learned that volatile liquids will evaporate in the presence of an inert, foreign gas exactly as if the latter were not present. To the water in the atmosphere is to be ascribed a *partial pressure* in virtue of which it distributes itself in the air. Exactly the same thing is true of hydrogen in the above experiment; at the start there was no hydrogen within the porous cell, so that the partial pressure of the hydrogen there was zero, and hydrogen on the outside, which was under atmospheric pressure, was forced into the cell

until the hydrogen pressure within was equal to that of the same gas without.

On taking away the beaker containing the hydrogen, the partial pressure of the hydrogen outside the cell became zero, and it was then necessary for hydrogen to pass outward through the porous wall until the partial pressure of the gas within had the same value; as fast as hydrogen escaped it passed upward in the atmosphere and fresh air took its place about the cell.

On account of this property that hydrogen shows of diffusing so rapidly, it is not advisable to attempt to keep a supply of the gas in the laboratory for any length of time, because it is almost sure to find some way to escape and exchange places, to some extent at least, with the outer air. There is, therefore, the constant danger of detonating gas being formed under such circumstances, so that the rule is to prepare a fresh supply of hydrogen whenever it is needed. Even the generator shown in Fig. 39 becomes filled with air after standing a few days, although the delivery tube may be left under water; and hence it is always necessary to test the purity of the gas, in the prescribed manner, before using it again.

**117. Ignition by platinum sponge.**— It is very remarkable that hydrogen, in spite of the violence with which it combines with oxygen when heated, can remain mixed with oxygen at ordinary temperatures without there being any evidence of a chemical reaction. It has been pointed out, in discussing the properties of oxygen (p. 121), that this inertia of chemical affinity at low temperatures makes it possible for combustible substances to exist in the atmosphere, and it has also been stated that certain substances, called catalyzers, are known which have the property of accelerating processes that otherwise take place so slowly at low temperatures as to be imperceptible. Platinum is such a catalyzer for hydrogen. Platinum is an expensive metal that is unattacked by most chemical substances; for this reason it is used to make vessels in which important chemical work is to be performed. It has a very high melting point and can be obtained in the shape of a fine, porous sponge by heating some of its compounds. This *platinum sponge* exerts a strong

catalytic effect upon the reaction between hydrogen and oxygen, and if a stream of hydrogen is directed against a piece of platinum sponge in the air, the oxygen in the latter will then combine quickly with the hydrogen and the heat of the reaction will suffice to heat the platinum to glowing, which in turn ignites the hydrogen. This behavior has been utilized in gas-lighting devices. Such an apparatus often contains a little platinum sponge which is heated to glowing when illuminating gas comes in contact with it, and the glowing platinum lights the gas.

**118. Drying of gases.** — It remains for us to prove by experiment that the hydrogen prepared from zinc and hydrochloric acid actually forms water when it burns. In such an experiment it is necessary, first of all, to *dry* the gas, *i.e.*, remove from it all the water vapor that comes from the dilute hydrochloric acid. To accomplish this, advantage is taken of the fact that certain substances tend to combine with water so strongly that they will remove it from gases. A white substance called *calcium chloride* is frequently used for this purpose, because it is convenient to handle and the material is relatively inexpensive. Fig. 41 shows one form of a "drying tube." At the bottom, where the tube begins to narrow, is placed a wad of cotton to prevent any of the dry substance from falling through, and a second wad likewise is placed on the top of the column of anhydrous calcium chloride; the tube is closed with a stopper through which a piece of open glass tubing is inserted. This drying tube is connected with the delivery tube from the hydrogen generator, and in this way the water vapor in the gas is removed.

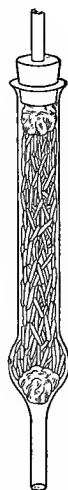


Fig. 41.

**119. Water from hydrogen.** — Pass hydrogen gas from the generator through the drying tube and then into a glass tube drawn out a little at the farther end. After testing the purity of the gas by holding an inverted tube over the open end for a moment and then bringing it near a flame, light it and regulate the flow so that the flame is not too high. It is best to fuse a little thin platinum foil into the end of the glass tubing

so that the hydrogen will burn pure. Otherwise the heat from the flame will melt the glass somewhat and certain constituents of the glass will be volatilized and impart a yellow color to the flame. Hold a large, dry beaker above the flame and note that drops of water will soon begin to condense on the surface of the glass. This shows that water is actually formed by the burning of hydrogen. By suitably constructed apparatus it is possible to collect any desired amount of this water. For other purposes, considerable quantities of water have been prepared in this way, and its properties have been found to coincide perfectly with those of natural water.

**120. Heat is evolved in the formation of water.** — If wires made of different metals are held in the hydrogen flame, it will be noticed that, in spite of its pale appearance, the flame is considerably hotter than that of a candle or even than that of illuminating gas. There is, therefore, a large amount of heat set free when the two elements hydrogen and oxygen combine. There is no other substance known of which an equal weight will give rise to as much heat as hydrogen when it burns.

A particularly high temperature is produced if the combustion of hydrogen takes place in the presence of pure oxygen. Since it is not safe to mix the two gases previously, as then the highly explosive detonating gas would be formed, a special burner has been devised by means of which oxygen and hydrogen are mixed in the proper proportion just at the time of combustion. Such a burner, commonly called the oxyhydro-

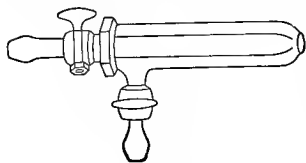


Fig. 42.

gen blowpipe, was invented by the English physicist, Daniell, and consists of two tubes, provided with suitable connections, placed one within the other and ending at the same place (Fig. 42). Hydrogen gas passes through the outer tube and oxygen through the inner one, and

the flow of both gases is regulated so that a pointed flame is obtained. The flame is colorless, is usually accompanied by a hissing noise, and is exceedingly hot.

If a piece of a watch spring is held in the flame, the steel soon begins to burn with scintillation. A platinum wire which melts in no other flame except that of the electric arc, melts to a round globule which is heated to a white glow and falls off after it has become large enough. A piece of lime emits a dazzling, bright light rivaling that of the sun. Various stones and other fire-resisting substances melt to vitreous masses; even quartz softens to a viscous mass which can be drawn out into threads.

Use is made of this very high temperature for various purposes. The bright light emitted by glowing lime is used for projection purposes with a stereopticon lantern and is sometimes called the Drummond light. The melting of platinum and quartz finds application in the manufacture from these materials of vessels which are used for chemical purposes because they resist heat so well and because they are not attacked by most chemical substances.

Instead of hydrogen, illuminating gas and the vapors of combustible liquids are sometimes used, because more convenient, although it is true that it is not possible thereby to obtain as high temperatures as when pure hydrogen is employed.

**121. Hydrogen as a reducing agent.** — The great tendency that hydrogen has to unite with oxygen and form water makes it possible for this element to act not only upon pure oxygen but also upon oxygen compounds. The latter are, in many cases, deprived of their oxygen on being heated with hydrogen. The union with oxygen is called an *oxidation* and the taking away of oxygen from the oxide is termed a *reduction*. Hydrogen, consequently, is a *reducing agent* toward such oxygen compounds.

This relation can be illustrated by an experiment with copper oxide. When metallic copper is heated in the air it becomes coated with a black layer of a brittle substance. By alternately heating a bundle of copper wires and then knocking off the oxide that forms, it is possible to prepare a quantity of it. If this black substance is placed in a glass tube and heated in a stream of hydrogen gas (Fig. 43) it soon assumes again the red color of metallic copper and at the same time a deposit of moisture will form on the colder parts of the tube.

This experiment can also be performed to show the weight relations between hydrogen and oxygen in water (*cf.* p. 133). If, for example, the copper oxide is weighed before beginning the experiment, the water formed carefully collected and weighed, as well as the amount of reduced copper remaining at the end of the experiment, all the necessary data are at hand. The loss in weight,  $A$ , which the copper oxide experiences, is equal to the weight of the oxygen that has been changed into water weighing  $B$ . The difference between the weights  $B$  and  $A$  represents the weight of hydrogen, and hence the ratio between

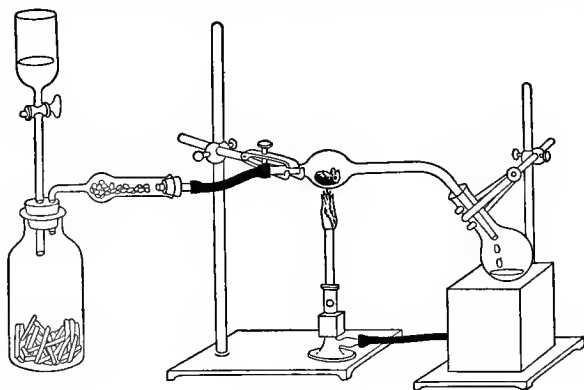


Fig. 43.

the oxygen and the hydrogen is  $A : (B - A)$ . Accurate experiments have shown this to be 1.008 : 8.000.

In like manner other oxides may be reduced; thus from yellow lead oxide metallic lead is obtained.

### § 17. WATER.

**122. The expansion of water by heat.** — The properties of water have already been described, because in many cases it is these properties that are taken as standards, or *units*, for measuring the same properties in other substances. The reason for this lies partly in the common and abundant occurrence of water and partly because it is not at all difficult to prepare



water that is practically pure, since most of the impurities in natural water are non-volatile; on distilling water these impurities remain behind.

Thus, for example, the density of water is taken as the *unit of density*. To be sure this density is not perfectly unchangeable but depends upon the pressure and temperature to which the water is subjected. The former influence is very slight, so that it is taken into consideration only in exceptional cases. By the pressure of an atmosphere water is diminished only 0.000,043 of its volume; one liter, therefore, would lose only 0.043 of a cubic centimeter in volume.

The influence of temperature is much greater. Between  $0^{\circ}$  and  $100^{\circ}$  the space occupied by a given amount of water increases about one-twenty-fifth, or 4 per cent, and the larger part of this increase takes place at the higher temperatures; a temperature of  $45^{\circ}$  is reached with only 1 per cent of expansion. Moreover, there is, in the case of water, the unusual behavior of contracting, rather than expanding, as the temperature changes from  $0^{\circ}$  to  $4^{\circ}$ , and at this last temperature water occupies its smallest volume. From this temperature upward it behaves like all other liquids and increases in volume with rise of temperature. This is the reason why the density of water at  $4^{\circ}$  C. is chosen as the standard in measuring densities; furthermore, at this point a very slight change in temperature has an inappreciable effect upon the density. These relations are shown very clearly in Fig. 44, in which the upper curve gives the *specific volume* (volume occupied by 1 g.) and the lower the *specific gravity* (weight of 1 cc.) of water at different temperatures. Note that the temperatures are marked along the line which is touched by both curves at  $+4^{\circ}$ , where the value of the specific gravity and of the specific volume is unity. The lower curve is the exact opposite to the upper one.

If a glass tube, like a thermometer in shape, were filled with water and the height of the latter read at different temperatures, it would be observed that the water level at first falls, as is to be expected, from  $0^{\circ}$  upward; but, contrary to the above plot, it does not begin to rise until a temperature of about  $+6^{\circ}$  is

reached. This is because the glass itself is expanding with rise of temperature, so that if the volume of the water were perfectly constant its level would slowly fall. At  $+4^{\circ}$  the rate of expan-

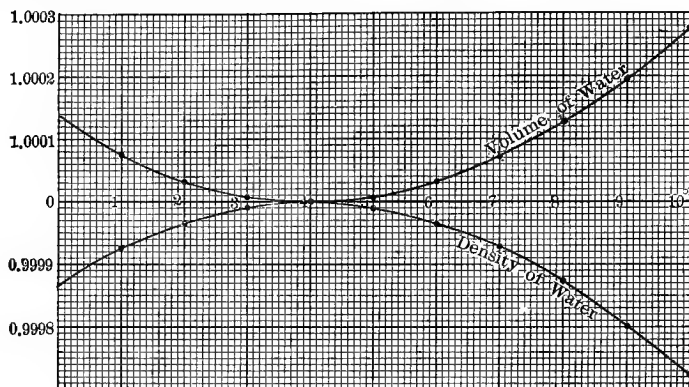


Fig. 44.

sion of the glass is greater than that of the water and at  $6^{\circ}$  it is practically the same as that of glass; at higher temperatures the water expands faster than glass, and the difference is more marked as the temperature rises.

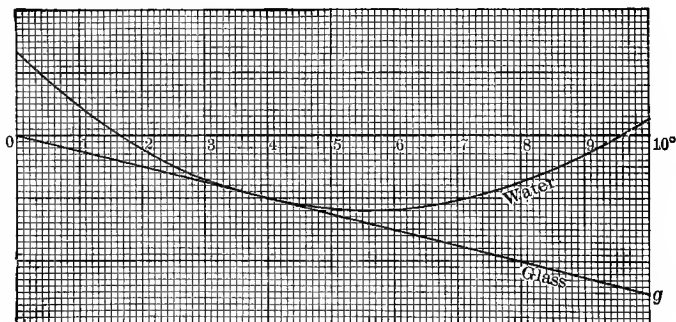


Fig. 45.

These relations may be illustrated graphically. Fig. 44 represented the change in volume as measured in a vessel which itself did not change with the temperature. In Fig. 45 the line  $Og$

shows the apparent diminution in volume which would take place in a *glass* tube provided the actual volume of the liquid did not change at all. If now the upper curve in Fig. 44 is plotted with this as a base line, the result will be a curve that represents the apparent change of volume which water experiences when measured in a glass vessel. In this case the lowest reading, *i.e.*, the smallest apparent volume occupied by one gram of water, is  $5.5^{\circ}$ .

The *coefficient of expansion of water*, or the change of a unit of volume per degree rise in temperature, is different at different temperatures. It is at first negative, *i.e.*, the volume becomes smaller with rise of temperature, is equal to 0 at  $+4^{\circ}$ , but above this temperature it assumes a positive value, and increases with rise of temperature. This is shown in the plot by the fact that the curve rises more rapidly as the temperature becomes higher.

**123. Importance of the maximum density.** — The fact that the maximum density of water is reached at  $+4^{\circ}$  C. is of great importance in nature, and if it were otherwise the conditions of existence upon the earth would be changed greatly. When, in winter, the water in lakes and ponds cools, heat is lost principally from the surface, where radiation and contact with the outer air occur. The colder water sinks downward and the warmer water rises from below to take its place. This, however, continues only until a temperature of  $+4^{\circ}$  is reached; when water is chilled below this temperature, it increases in volume, becomes lighter, and therefore remains at the surface. Finally ice forms on the surface and remains there because ice itself is considerably less dense than the water from which it is formed. If the water is of any depth, it is protected from freezing by this coating of ice, as it retains for a long time the temperature of maximum density,  $+4^{\circ}$ , and only loses it very slowly by conduction up through the ice.

If water behaved like other liquids, it would all be cooled down to the freezing point, then the solid would form and sink to the bottom and finally the whole mass of liquid would freeze. Whereas now a relatively small amount of heat serves to melt the ice coating in the spring, it might then happen that the entire

heat of summer would not suffice to melt all the ice in a large body of water, for the upper layers of water would conduct heat very slowly to the ice beneath. In winter, fish could no longer exist in regions where they are now abundant.

Water does not separate into layers of different densities in rapidly moving streams but is kept thoroughly mixed. In such cases water may be cooled to  $0^{\circ}$  and ice will not form on the surface but at the bottom where inequalities in the bed of the stream serve, as is usually the case in freezing liquids, to start the crystallization. When the amount of ice formed in this way becomes so large that it will no longer adhere to the bottom, it rises to the surface and usually carries with it more or less dirt, roots, etc. Such ice is called "ground ice" or "anchor ice."

**124. Ice.** — We have already learned that water passes at  $0^{\circ}$  into the solid form, and have made use of this as a starting point for the measurement of temperatures. Water, unlike all other substances, is denser in the liquid than in the solid form; or, in other words, it expands on freezing. Ice at  $0^{\circ}$  has a density of 0.916. An iceberg floating on the water, therefore, has nearly one-eleventh of its total volume above the surface of the water; in all other cases a solid substance in contact with its own liquid rests at the bottom. Probably the peculiarity of expanding on freezing is closely related to the property that water shows of expanding when cooled below  $+4^{\circ}$ .

The boiling point of water, under an atmospheric pressure of 76 cm. is at  $100^{\circ}$  and increases about  $0.37^{\circ}$  for each additional centimeter of mercury pressure; in fact the boiling point of water can be computed on this basis for pressures varying not more than 2 cm. from the normal. Even at  $0^{\circ}$  water has an appreciable vapor pressure amounting to 0.46 cm. of mercury. The vapor pressure of ice is the same at this temperature.

**125. The action of water upon the earth's surface.** — Inasmuch as water occurs in such large quantities upon the surface of the earth and practically penetrates and influences everything with which it comes in contact, it plays a varied and most important part in almost all phenomena. In the first place, it is found in the three different states of aggregation, as vapor,

liquid, and solid. In the last state it always exists at the poles and at great heights on the configuration of the earth's surface. Whereas stones always tend to obey the force of gravity and *fall lower* in the form of larger or smaller fragments, ice is the only solid substance (outside of masses that are projected as a result of volcanic activity) that regularly *builds itself up* in consequence of snowfall. To be sure the ice that rests upon the mountain top is influenced by the action of gravity and its downward movement is favored by a property that is not met with in other minerals. Mountain ice moves downward as if it were a slow stream of viscous material, and forms *glaciers* in the bed of which it flows like the water in a brook, only ever so much more slowly. This ability to flow is closely related to the fact that ice is less dense than water and expands on freezing.

Whereas substances that contract on freezing, and therefore expand on melting, experience a rise in the melting point when subjected to pressure, it is exactly the reverse with ice; *it melts at a lower temperature in proportion as pressure is exerted upon it*. This effect is, indeed, extremely slight and amounts to only  $0.0073^{\circ}$  for a pressure of one atmosphere. In the case of a solid, like ice, however, the pressure exerted upon it may be very great, especially when concentrated upon corners or edges, for it is inversely proportional to the size of the surface upon which the pressure is exerted. Consequently, the ice melts at the places exposed to high pressures, then the water releases the pressure and ice forms again. In this way the ice appears to be plastic, inasmuch as it can be shaped by pressure.

A very good idea of this behavior is obtained if a block of ice of a few cubic decimeters in size is supported between two chairs and upon it is placed a fine wire to which a heavy weight is attached (Fig. 46). The wire presses into the ice and at the end of a few hours it cuts entirely through and the weight falls to the floor; as fast as the ice melts the wire passes through the cold water, which, when the pressure is released, freezes again, so that at the end of the experiment the whole

block of ice appears unchanged. Only a fog of air bubbles shows the path taken by the wire through the ice. The experiment succeeds at different temperatures, but is most convincing when performed in winter out of doors with the temperature a few degrees below the freezing point.

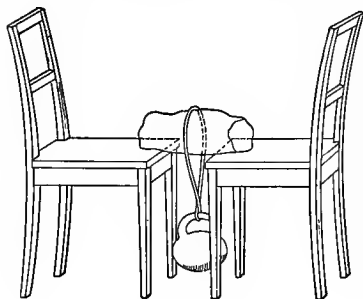


Fig. 46.

Although at the present time the formation of glaciers, with its attendant abrasion upon the substratum and its transportation of neighboring rocks, is restricted to a relatively small range of territory, there was a time when a far greater extent of the earth's surface was exposed to the action of glaciers. Thus gigantic glaciers were formed in Scandinavia and passed onward toward the North German plain, and even to-day accurate examination of drift blocks, by taking a thin section of the rock and observing it under the microscope, unquestionably proves the northern origin. Glaciers end when the melting accomplished by the warmth of the air balances the pressure on the ice imparted by the flow. Both causes are subjected to various influences, so that the end of the glacier in the valley moves slowly backward and forward in the course of the year. From this point onward the water flows in the liquid state to the ocean.

Another, much larger amount of water falls upon the earth in the form of rain, and this is likewise made to flow toward the ocean as a result of the action of gravity. On its way the stream has many effects, partly mechanical and partly chemical in nature.

The mechanical effect consists chiefly in the demolishing of stones. In this respect the expansion of water on freezing is very efficient. When water freezes in the cracks and crevices of rocks it presses hard against the confining walls and eventually breaks them. By this means large amounts of debris are an-

nally loosened from the rocks of the mountains; part of this debris is precipitated into the valleys and part is carried along with the water. If, during the warm seasons of the year the masses of ice on the mountain tops melt, then the brooks swell, flood their banks, and carry with them all the pieces that were loosened during the previous winter by the action of ice. In this process the masses of stones constantly tend to become smaller and smaller and there is an elutriation effect (*cf.* p. 21) by which the finest particles are carried farthest and the coarsest particles remain nearest the place of origin. Thus the cascades advance the bed stone, the brooks the gravel, the rapid streams the sand, and the slower ones merely the mud. When this slime comes in contact with sea water, the effect of the salt is to deposit the sediment as a fine mud, and in this manner the well-known three-cornered islands, or deltas, are formed and tend constantly to increase so that they must be attended to regularly or navigation will be obstructed.

To illustrate this important geological phenomenon take some pure clay (kaolin) and mix it with distilled water to make a very fine mud, mix one portion of this with more distilled water, and another part with a solution containing common salt and a little magnesium chloride to imitate the water of the ocean. While the solid mixed with distilled water remains in suspension for a long time, that diluted with brine settles quickly to the bottom.

Besides the mechanical action, which consists essentially in breaking up the rocks and separating the fragments by carrying them onward, the water also exerts a deep-seated chemical effect upon the stones with which it comes in contact. In order to understand these effects, however, it is necessary to know more concerning the nature of the stones themselves, so that it cannot be discussed further at this place.

**126. Cycle of water.** — All this water is raised up into the atmosphere as vapor by means of the heat of the sun, and from the skies it falls again to cause all of the above-mentioned effects. The formation of water vapor takes place wherever water comes in contact with the sun's rays, whether this be on the surface

of the ocean, on rivers, lakes, etc., or whether upon the vegetation of the solid earth. For water is, by weight, the chief constituent of all kinds of life, playing the parts, as on the earth's surface, of a solvent and of a transporting agent. Since water vapor is only 0.62 times as dense as air, it always tends to rise at the places where it is formed, and hence evaporation takes place more quickly than if the vapor rested in the form of a dense layer at the bottom of the atmosphere, for the moist air that rises is constantly being replaced by drier and heavier air. Inasmuch as the upper atmosphere gradually becomes colder, obviously a place will be reached eventually where the air is saturated or supersaturated with moisture and, as a result, water descends upon the earth again in the form of rain or snow according to the temperature. In the meantime the wind causes a still further transportation of the vapor, and in this way there is an equalization of the water distribution upon the earth's surface, although, to be sure, there is a strong preference toward the cold regions near the two poles. Simultaneously with this distribution of substances there is also an important equalization of energy, for the vapor carries with it a considerable amount of heat that is given up to those regions where the liquefaction takes place. In this way, heat is carried to those cold and dry regions where it is most needed, and in this way the habitable parts of the earth are stretched out farther toward the poles.

It is evident, therefore, that water as a whole takes part in a very wide cycle; it arises in the form of vapor from the seas and from the valleys, is deposited upon the heights in the form of rain or snow, and passes onward ever downward until finally it reaches the sea again. In this cycle the water, while in contact with the earth, not only takes part in the disintegration of rocks but is also constantly exerting its natural solvent power upon all soluble substances with which it comes in contact. These, however, are for the most part non-volatile, so that they cannot participate further in the cycle, but collect in the ocean, as the deepest regions to which they are carried. The salt content of the ocean is thus produced, and, under the prevailing conditions, must ever tend to increase constantly, although very slowly.



According to this, the salt content must be greater in proportion to the evaporation. The Mediterranean Sea, with its very strong evaporation, has a salt content of 3.7 per cent, whereas the Baltic, with its abundant tributaries and its lesser evaporation, because of its northern position, has a salt content of only from 0.3 to 0.8 per cent.

**127. Electrical energy.** — Up to this point we have considered only *heat* as an agent for breaking down compounds into the elements. Another very active agent is found in the *electric current*. Both heat and electricity are *forms of energy, i.e.*, they can each be obtained by the application of mechanical work, or, conversely, may be transformed back into mechanical work. Thus in the steam engine heat is transformed into work and, conversely, heat is produced by work in the friction of every bearing, and by the lighting of every match.

We are forced to conclude, moreover, that in the substances which are capable of entering into chemical combination with liberation of heat there must be already present some kind of energy. This follows because there is a general law stating that energy can be neither created nor annihilated; whenever, therefore, energy appears in any form it must be as a result of a transformation of some kind of energy that was already present. Accordingly, there exists *chemical energy* which is present in substances and is usually given up to some extent when they combine with one another. All combustible substances unite with oxygen with evolution of considerable heat; there is, therefore, chemical energy present in such substances.

As regards the energy of the electric current, it may result from mechanical or from chemical sources. Thus in power plants the electricity of the dynamos is obtained by the expenditure of mechanical work. The latter is taken usually from a steam engine, which in turn is dependent upon the chemical energy contained in the fuel. In such cases as this, then, there is an *indirect* transformation of chemical energy into electrical energy; heat energy and mechanical work represent intermediate stages in the transformation. It is, however, possible to transform chemical energy *directly* into electrical energy; this is

accomplished in the voltaic cell. Such a cell is formed by bringing together substances which act upon one another if an electric current passes through them. Thereby they drive the current on whenever this is possible, *i.e.*, when the circuit is *closed*. For this purpose it is necessary to connect certain parts of the circuit, the *poles*, by means of a conductor of electricity.

**128. Conductors of electricity.** — There are two kinds of conductors. The first kind includes metals and certain similar substances such as carbon. If an electric current passes through them nothing happens except that some of the electric energy is transformed into heat energy and the conductor becomes hot. Upon this property depends the construction of the well-known incandescent electric lamps, which contain filaments of carbon or of a metal such as osmium, tantalum, or tungsten, and these filaments are so placed that they are heated to bright glowing when introduced into a suitable electric circuit.

The other kind of conductors consist of *dissolved* or *fused* compound substances. These are not only heated when a current passes through them, but they also experience at the same time a chemical decomposition; one component appears at the place where the electric current enters and another where it leaves. The constituents that are set free may be elements or they may be compounds; it all depends upon the nature of the original substance. All compound substances do not conduct electricity in this way, and some of them practically do not conduct it at all; they are called *nonconductors* or *insulators*. We shall subsequently learn the property that makes it possible for a substance to conduct electricity when in a dissolved or molten condition; such substances all belong to the class of "salts," the term being used in a broad sense and including acids and bases. The energy of the electric current on passing through a conductor of this class is transformed into chemical energy, which is possessed by the constituents set free.

Conductors of this kind are called *conductors of the second class*, or *electrolytes*; the decomposition brought about by means of the electric current is termed *electrolysis*, and the places where the current enters and leaves the electrolyte are termed

*electrodes.* In carrying out an electrolysis it is always necessary to bear in mind that the chemical constituents of the electrolyte when set free are very prone to enter into chemical combination with the electrodes, unless the latter are made of some substance which resists such action.

**129. Electrolysis of water.** — Water itself is a poor conductor of electricity; it is not an electrolyte. If, however, certain substances are added, as for example sodium hydroxide, it conducts very much better and the constituents of water are then set free at the electrodes. Just how this is possible will be explained later, but at present the only essential thing to know is that it is actually *the elements of water* that are the final products in such an electrolytic decomposition, or electrolysis.

Conduct the electric current, which can be obtained from a direct-current lighting system by interposing a lamp, through a solution of sodium hydroxide (Fig. 47). In this case the electrodes may be of iron or of nickel. The apparatus consists of a beaker to hold the solution in which the electrodes are immersed. To make sure that the current enters and leaves the solution only from the electrodes, the remaining parts of the circuit are insulated. As soon as the circuit is closed there takes place at each electrode an evolution of a gas which can be collected in the usual manner. Collect the gases separately as shown in the drawing, and prove that one will ignite and the other cause a glowing splinter to take fire; the gases are, therefore, actually hydrogen and oxygen.

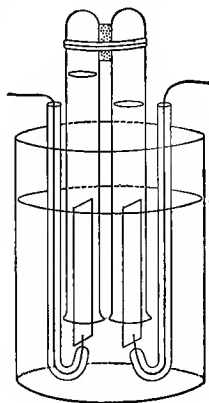


Fig. 47.

The electrolytic decomposition of water may be used as an experiment to show in what proportions by volume the two gases are evolved; this is naturally the same relation in which they unite to form water. It is at once noticeable that much more hydrogen than oxygen is evolved, and accurate measurement proves that *two volumes of hydrogen are set free with one of oxygen.*

From this, again, the density of hydrogen can be computed. We have already learned that 8 parts by weight of oxygen combined with one part by weight of hydrogen to form water; since electrolysis shows that one part by weight of hydrogen occupies twice as much volume as the 8 parts by weight of oxygen, it is evident that the density of hydrogen is one-sixteenth that of oxygen.

As oxygen has the combining weight of 16 and hydrogen that of 1, it follows that the *gas densities stand in the same relation to each other as do the combining weights*.

The question naturally arises whether this is always the case. The answer is that it is true in some cases and not true in others. In the latter cases, however, the gas densities stand in some simple multiple relation to the combining weights, so that, at all events, there is a close relation between the two values. In order to understand this fully, it is first necessary to become acquainted with the properties of more elements and compounds and then come back to the question.

**130. Water as a solvent.** — The fact that water is a common solvent has already been brought out in a number of experiments, for many of them have been carried out in aqueous solutions. This practice is comparatively modern, for in olden times most chemical experiments were carried out in the dry way, as in metallurgy, and chemical processes were made to take place by heating a mixture of the reacting substances. At the present day we know that by virtue of the solvent properties of water chemical reactions take place more readily in it than in any other solvent. Thus the historical development has proved to be theoretically justified.

This action rests upon the fact that the solutions of a large class of substances, called "salts" in a very general sense, are all electrolytes. Water in a pure state conducts the electric current only slightly (p. 155); if any soluble salt-like substance is added to the water, its conductivity is greatly increased. To illustrate this, connect a voltaic battery (several so-called "dry cells" will answer) in circuit with an electric bell and with two parallel electrodes insulated from one another (Fig. 48).

Insert the two electrodes into a beaker of distilled water and note that not enough current passes through the circuit to ring the bell. Repeat the experiment, using, instead of water, dilute solutions of common salt, of hydrochloric acid, or of potassium nitrate, etc.

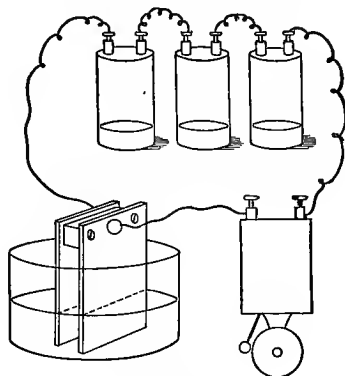


Fig. 48.

In the same way solutions of all kinds in benzin, alcohol, and other solvents can be shown to be nonconductors, so that the peculiarity of water in this respect is easily demonstrated. These relations are of great theoretical importance and will be mentioned again.

## CHAPTER VI.

### HALOGENS AND SALTS.

#### § 18. CHLORINE.

**131. Properties of chlorine.** — The element chlorine, like oxygen, can be purchased in steel cylinders, in which it is present not in the gaseous condition but in the form of a liquid. It boils, to be sure, at  $-33.6^{\circ}$  under atmospheric pressure, but at  $+20^{\circ}$  it has a vapor pressure of only 6.6 atmospheres, so that it can be liquefied comparatively easily. It is a yellowish-green liquid, of somewhat oily appearance, which at once begins to boil in the air; thereby its temperature is reduced to  $-33.6^{\circ}$ . The vapor from this liquid, *chlorine gas*, shows the same yellowish-green color, although, corresponding to its much lower density, it is much paler, and is an extremely poisonous and chemically active substance. Like oxygen, chlorine can combine with nearly all other elements; it differs from oxygen, however, inasmuch as this tendency toward combination is shown even at *ordinary temperatures*. Herein lies the reason for its poisonous nature; it acts chemically upon the tissues of the body and destroys them.

In nature chlorine does not occur in the free state, but its compounds are very widely distributed. Ordinary table salt is a compound of chlorine with the light metal sodium, and its chemical name is sodium chloride. As is well known, sea water is chiefly a dilute solution of common salt. Chlorine combines with other metals and forms compounds that are more or less similar to table salt and which, therefore, are also called salts. Since, moreover, there are other substances that likewise give similar compounds with the different metals, it has been found advisable to broaden the conception still more, and the term "salt" now includes all such compounds. This conception will be explained more fully a little later.

**132. Preparation.** — Another substance containing chlorine is *hydrochloric acid*,<sup>1</sup> which we have already used. It is a compound of chlorine and hydrogen and is called, therefore, *hydrogen chloride*; it may serve as the starting material for the preparation of chlorine in the laboratory. For this purpose it is evident that hydrogen must be withdrawn from the compound. Since its decomposition by heat meets with the same difficulty as in the case of water (p. 134), it is necessary to make the hydrogen combine with some other element, or decompose the hydrogen chloride by “selective affinity.” Oxygen will serve as this other element, and it is best to use it in the form of a compound. The latter must be capable of combining with the hydrogen without at the same time combining with all the chlorine. Such a compound is pyrolusite, which we have used in the preparation of oxygen.

The chemical name for pyrolusite is *manganese dioxide* and it is, as its name suggests, composed of one combining weight of manganese with two of oxygen. The second combining weight of oxygen is capable of combining with the hydrogen in hydrogen chloride, meanwhile letting the chlorine escape in an uncombined state.

Place a little manganese dioxide in a test tube and heat it with some hydrochloric acid. The liquid soon becomes colored a dark brownish green and begins to give off a very unpleasant odor, which is that of chlorine. This is so easily recognized by any one who has once smelled it that the nose itself may be said to act as a reagent in testing for chlorine. Since it is desirable, also, to have a *visible* test, the property that chlorine has of bleaching dyestuff may be utilized. For example, litmus, which is so commonly used to indicate the presence of acid (p. 123), is bleached by chlorine. To show this, hold a piece of litmus paper in the test tube from which chlorine is being evolved; without coming in contact with the liquid in the tube but merely with the gas, the paper soon becomes white.

If it be desired to prepare larger amounts of chlorine, this should be done under a well-ventilated hood, so that any escaping gas

<sup>1</sup> The hydrochloric acid of the laboratory is an aqueous solution, but the name properly belongs to the dissolved substance itself.

will not contaminate the air of the laboratory. An apparatus such as is shown in Fig. 49 is suitable for the experiment. The flask, which is fitted with a two-holed stopper carrying

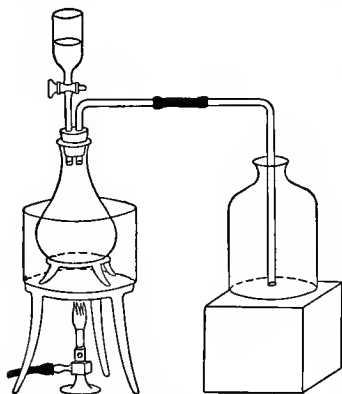


Fig. 49.

a dropping funnel and a gas-delivery tube, is about two-thirds filled with manganese dioxide and heated in a water bath. That is to say, the flask is placed in a kettle containing water, and is supported so that it does not touch the bottom or sides of the kettle; otherwise bubbles of steam would form under the flask and perhaps break it. If the flask were heated in a free flame, it would become very hot at certain places, and if the cold acid should come in contact with such places

the flask would be likely to break and chlorine escape into the room. In a water bath the glass cannot be heated above the boiling point of water, and, moreover, the heat is applied uniformly from all sides. Water baths, therefore, are used whenever it is desired to heat uniformly and not too hot. If it is desired to heat in the same uniform manner to a temperature above  $100^{\circ}$ , oil is used instead of water, and in this way an oil bath is obtained.

If hydrochloric acid is allowed to drop upon the heated pyrolusite, it will be noticed that the flask soon becomes filled with greenish-yellow chlorine gas. From the way in which it rises in the flask it is obvious that the gas is much heavier than air; as a matter of fact it is 2.5 times as dense. It should not be collected over water, as was done in the previous experiments with gases, because chlorine is quite soluble in water; it is best to lead it, by means of a long delivery tube, to the bottom of a dry bottle, placing a sheet of white paper back of the bottle so that the process can be watched. Gradually the heavy, yellowish-green vapors will rise in the bottle. When a bottle is



filled, it is replaced by another, and the diffusion of the gas from the filled bottle is prevented by covering with a small glass plate the under side of which is coated with vaselin.

The gas may also be collected in a bottle half filled with water, and by shaking the bottle its dissolving is facilitated. At the room temperature three or four volumes of chlorine will dissolve in one volume of water. The solution, called *chlorine water*, has the greenish color of chlorine, as well as its odor and bleaching power.

**133. Compounds.** — The following experiments, illustrating the readiness with which chlorine enters into combination with other elements, can be made with gaseous chlorine; the experiments must be performed under the hood or out of doors. Shake powdered antimony into a jar of chlorine gas and notice the shower of sparks formed; enough heat is evolved by the combination of antimony with chlorine to make the solid glow. A white mass, called antimony chloride, is deposited in the flask. Throw a ball of Dutch metal, which consists chiefly of copper and zinc, into another bottle of the gas; it likewise glows and the corresponding chlorine compounds are formed; the residue has a brown appearance and dissolves in water with a green color (copper). Colored flowers on being thrown into a bottle of chlorine become white. Phosphorus, when lowered into a bottle by means of an iron spoon, takes fire spontaneously and burns with a pale greenish flame to phosphorus chloride. This last experiment is a somewhat dangerous one to make.

**134. Chlorine water.** — By means of chlorine water it can be shown that even gold, which otherwise enters into chemical combination only with difficulty, will unite with chlorine. Place a piece of pure gold leaf in chlorine water and notice that the metal disappears entirely after a time, forming gold chloride, which is soluble in water, and forms a yellow-colored solution. Moreover, chlorine acts upon bad-smelling liquids, *e.g.*, decaying solutions of glue or gelatin, in such a way that the foul smell is lost. This action is spoken of as *disinfection*, and chlorine is often used for destroying odors that arise from putrefaction. Similarly it kills the minute germs of injurious forms of life, the *bacilli*, etc.,

but its use in this direction is limited by the fact that it also acts injuriously upon many other things and is poisonous as well toward higher forms of life.

A very interesting experiment is the following: fill a bottle with chlorine water, close it with a stopper carrying a short piece of glass tubing, support the bottle in an inverted position over a dish of water, and place it in direct sunlight (Fig. 50).

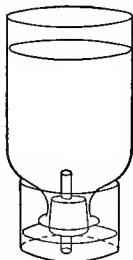


Fig. 50.

Soon bubbles of gas begin to form in the bottle and a part of the water is forced out. When the evolution of gas has ceased all the chlorine will have disappeared and the gas that has been collected in the top of the bottle is oxygen; prove this by testing with a glowing splinter. Test also the liquid in the bottle with a strip of blue litmus paper. Under the action of the sun's rays, the chlorine has united with the hydrogen of water in such a way that hydrochloric acid has been formed and the oxygen of water set free. Here we have a chemical reaction brought about by the action of light. We shall subsequently learn that a similar process takes place in green leaves, likewise with evolution of oxygen.

Chlorine causes the production of oxygen from water even more readily when the oxygen instead of being allowed to escape is brought into contact with another substance upon which it can act or with which it can combine. Hereby chlorine, in the presence of water, plays the part of an oxidizing agent and as such finds extensive application in chemical reactions. In such cases the coöperation of light is not necessary.

**135. General character.** — All these experiments show that chlorine acts not only upon free elements but also upon chemical compounds. The decolorization of dyes depends chiefly upon the fact that the elements in the dyestuff, particularly hydrogen, unite with chlorine and thus the natural color is destroyed. By reason of this marked activity of chlorine it is hardly to be expected that chlorine will be found in nature in the free state, because there are so many opportunities for it to enter into combination. In fact, free chlorine is only found in con-

junction with volcanic activity, where the escaping gases sometimes contain chlorine; this, however, very soon passes over into a state of chemical combination.

The compounds of chlorine with other elements are very diverse in nature. This is especially true because chlorine, like oxygen, often unites with an element in more than one proportion. In order to distinguish this in the name of the compounds, it is customary, in English, to affix the termination *ous* or *ic* to the name of the metal. Thus ferrous chloride denotes a compound having less chloride than ferric chloride, and cuprous chloride contains less chlorine than cupric chloride. A compound with more chlorine still is called a *perchloride*, and when four chlorides are known, that with the least chlorine is the *subchloride*.

136. **Hydrogen chloride.**— Prepare a hydrogen generator, as shown in Fig. 51, and pass the hydrogen through a drying tube into a delivery tube which at the end is lined with platinum foil to form a gas burner. Light the hydrogen, after observing the usual precautions, and lower the flame into a bottle of chlorine gas. The color of the flame, which was a pale blue in the air, changes to a light green, but the burning continues. Since the bottle contains only chlorine, it is evident that the two elements hydrogen and chlorine unite with each other in precisely the same way as hydrogen and oxygen. The experiment should be carried out under the hood, as a part of the chlorine gas is wasted. Eventually the flame dies out and the bottle is filled, for the most part, with a colorless gas, although usually a little chlorine remains, having escaped the combination with hydrogen. At the mouth of the bottle, where the new gas comes in contact with air, fumes

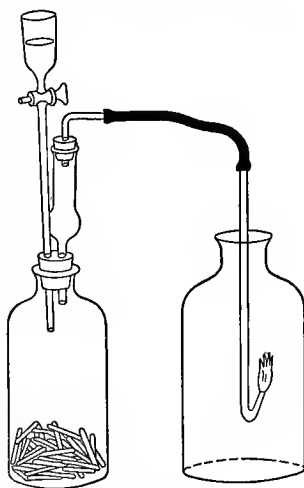


Fig. 51.

are noticeable and they become more distinct on blowing against the mouth of the bottle; the fumes are formed by the gas coming in contact with the moisture in the air.

When hydrogen burns in an atmosphere of chlorine, a *colorless gas* called *hydrogen chloride* is formed. Whereas hydrogen and oxygen unite in the proportion of two volumes of hydrogen and one volume of oxygen to form two volumes of water, one volume of hydrogen combines with one volume of chlorine to form two volumes of hydrogen chloride.

On mixing together chlorine and hydrogen, *chlorine detonating gas* is formed, and here again, as with ordinary detonating gas, the combination of the two elements does not take place spontaneously at room temperature but can be brought about by certain external causes. If the mixture is ignited by a flame or an electric spark, an explosion takes place as with ordinary detonating gas. In spite of the readiness with which chlorine forms compounds even at the ordinary temperature, direct combination with hydrogen is sluggish.

This is true, however, only when the mixture is kept in the dark or in very dim light. If the mixture is exposed to a strong light the combination of the two elements at once begins to take place and soon enough heat is generated so that the process is propagated rapidly throughout the whole mass and an explosion results. If the light is dimmer, the heat is dissipated more and combination takes place slowly without the mixture becoming hot enough at any time to cause an explosion. This dependence of the velocity of a chemical reaction upon the amount of illumination has been used as a basis for constructing a chemical photometer, *i.e.*, an instrument for measuring the amount of light. Such a photometer is not very convenient, however, so that it has served merely for scientific purposes.

This is, then, another case where the chemical effect of chlorine is accelerated, or brought into play, by the influence of light. Many other reactions of chlorine upon various substances are influenced in the same way, so that the possible effect of light must always be taken into consideration in working with chlorine.

**137. Acids.** — Hydrogen chloride, which was formed by the combustion of hydrogen in chlorine, is a colorless gas and differs from all the other gases that have been mentioned up to this point in being absorbed to a very great extent by water. If the bottle in which hydrogen chloride formed is inverted and its mouth placed in some water, the latter will be sucked quickly into the bottle. For, as the gas dissolves in water, an empty space is formed in the bottle and consequently the water is driven in by atmospheric pressure. The bottle will not quite fill itself with water, simply because a little air entered the bottle during the experiment in which the hydrogen chloride was formed.

The very dilute solution of hydrogen chloride prepared in this way at once turns blue litmus paper red, showing the presence of an acid. Hydrogen chloride, in fact, is an acid and possesses the pronounced characteristics of this class of substances. Now as another experiment, which may also be utilized for recognizing acids, throw a little piece of magnesium into another portion of the solution. A gas is evolved that can be identified as hydrogen. It is, in fact, a property of all acids to generate hydrogen when placed in contact with magnesium. Magnesium is by no means the only metal that shows this behavior, for we have already generated hydrogen by the action of hydrochloric acid upon zinc (p. 135). Magnesium, however, does this work more rapidly and more distinctly, even with very dilute and with very weak acids, so that it serves better as a test for this class of substances. The nature of the reaction, however, is the same with magnesium as with zinc; the chlorine in the hydrochloric acid combines with the metal, and the hydrogen is set free.

From the fact that all other acids likewise evolve hydrogen when treated with magnesium, the conclusion must, therefore, be drawn that all acids contain hydrogen replaceable by magnesium. This is, in fact, true. *All acids are hydrogen compounds.* The converse of this last statement, however, is not true, because many hydrogen compounds are not acids. Thus water is a compound of hydrogen, as we have learned, and water is not an acid, for it does not redden blue litmus nor does

it evolve hydrogen with magnesium (*cf.* p. 189). Therefore, a more accurate definition of an acid is:

*Acids are those hydrogen compounds which evolve hydrogen when treated with magnesium.* Such substances also redden blue litmus paper. Both these tests are always made in aqueous solutions.<sup>1</sup>

**138. Hydrochloric acid.**—Hydrogen chloride gas can be transformed into a liquid by suitably lowering the temperature and increasing the pressure, but the boiling point of this liquid is  $-83^{\circ}$  at atmospheric pressure, and its pressure is 41 atmospheres at  $18^{\circ}$ . It is clearly not at all convenient to handle this substance in the liquid state. For all ordinary purposes, therefore, the aqueous solution of the gas is used under the name of *hydrochloric acid* (also called muriatic acid), and in this form it was known to the alchemists of the Middle Ages. In the pure state, hydrochloric acid solution is a colorless liquid which is denser than water, according to the amount of gas in solution. The solution fumes in the air if it contains more than 20 per cent of hydrogen chloride by weight. The strongest acid of commerce contains about 39 per cent. The crude acid is often yellow, the color being usually caused by the presence of ferric chloride but sometimes by organic matter.

The fuming of hydrogen chloride, and of the concentrated solutions when exposed to the atmosphere, is due to the fact that the solution containing 20 per cent of hydrogen chloride has the lowest vapor pressure and consequently the highest boiling point of all possible aqueous hydrochloric acid solutions. From the boiling point of pure water, which is at  $100^{\circ}$ , the boiling point of the dilute hydrochloric acid rises at first in proportion to the concentration, until a temperature of  $110^{\circ}$  is reached when the acid has a concentration of 20 per cent; the boiling point can rise no further, and a more concentrated acid begins to boil at a lower temperature. From solutions containing less than 20 per cent hydrogen chloride, water, or a more dilute acid, distills off first; whereas from solutions containing more than 20 per cent hydrogen chloride, the vapors that first come off contain less and less water and more hydrogen chloride. From this the characteristic

fuming of the concentrated acids and of pure hydrogen chloride can be explained.

Although hydrogen chloride is a gas at the ordinary temperatures, and is not visible, it is transformed by contact with water vapor (likewise invisible) into the (20 per cent) solution of lowest vapor pressure, and this is precipitated from the atmosphere in the form of minute drops as a cloud or fog, because the vapor pressure of this solution is so small at the prevailing temperature that only a very little of it can remain in the atmosphere in the form of a gas. Similarly, in the case of the more concentrated solutions of hydrochloric acid, the vapors arising consist principally of hydrogen chloride, and this colorless gas undergoes the above-described transformation when it comes in contact with the water vapor of the atmosphere. The more dilute solutions, on the contrary, lose chiefly water by evaporation, and vapor will be given off only as long as the amount of water already present in the air will permit; they, therefore, give no cause for fuming.

Quite similar relations occur with other gases or readily volatile acids, and whenever we find that such a substance, or its concentrated aqueous solution, fumes in the air, we shall be justified in at once concluding that it yields a solution of moderate concentration which has the lowest vapor pressure of all the solutions of this substance, and that it forms such a solution when the substance itself, as gas or vapor, comes in contact with moist air. The fumes will be stronger in proportion to the prevailing humidity (p. 88) and do not appear at all in perfectly dry air.

The aqueous solutions of hydrochloric acid exhibit to a marked degree all the properties of an acid. Add a few drops of the ordinary laboratory reagent to some water in a beaker and stir well, because the heavier acid at first goes to the bottom of the beaker. Taste the very dilute solution and note that it is distinctly sour. Test it also with blue litmus paper, and again with magnesium powder. Such dilute acid is not poisonous; on the contrary, the stomach itself secretes a very dilute solution of hydrochloric acid and its presence is essential for the proper digestion of the food. If the stomach for any reason loses the ability to secrete the acid, digestion suffers, and in such

cases it is necessary to administer a dilute solution of hydrochloric acid. In a concentrated condition, however, the action of the acid is so strong that it attacks the tissues and is, therefore, a poison. Many other substances that are used in medicine have a healing effect when used in not too great a concentration, but become very injurious if taken in large quantities.

On account of its marked acid properties, hydrochloric acid finds an extensive application in chemical industries because it is one of the less expensive acids. Its use, however, depends for the most part upon chemical reactions which we cannot study till a little later, so that they will not be described at this point. Similarly, it is best to postpone the explanation of the technical preparation of the acid from common salt until we have become acquainted with other substances that take part in the process.

**139. Density and content of solutions.** — The hydrogen chloride content of an aqueous solution of hydrochloric acid can be determined by the density, because the latter becomes greater and greater as more of the gas is dissolved in the water. To be sure, the increase in density is not strictly proportional to the concentration of the acid, and on mixing concentrated acid with water, the total volume does not remain unchanged but becomes smaller. In other words, a contraction in volume takes place upon dilution of hydrochloric acid.

On account of this contraction, which is dependent upon the concentration and the temperature, it is necessary to measure the relation between density and acid content in different solutions by direct experiments. Since it is out of the question to investigate every imaginary concentration, measurements are merely made in quite a number of solutions, of which the differences in concentration are kept as uniform as possible and intermediate values are based upon the law of continuity (p. 53). This is most readily done by making a plot, laying off the densities as horizontal distances and percentage contents as vertical distances, and connecting the points thus obtained by a continuous line (Fig. 52). Since all the densities are greater than one, the plot begins at this point. Thus on the plot instead



of measuring off 1.125, only the distance 125 is shown; Fig. 52 would have to be 50 cm. longer if the plot were to be drawn so that the dispensable area from 0 to 1 were to be shown. It is evident from the curve (in this case a straight line) that the densities are nearly proportional to the percentage content of the acids.

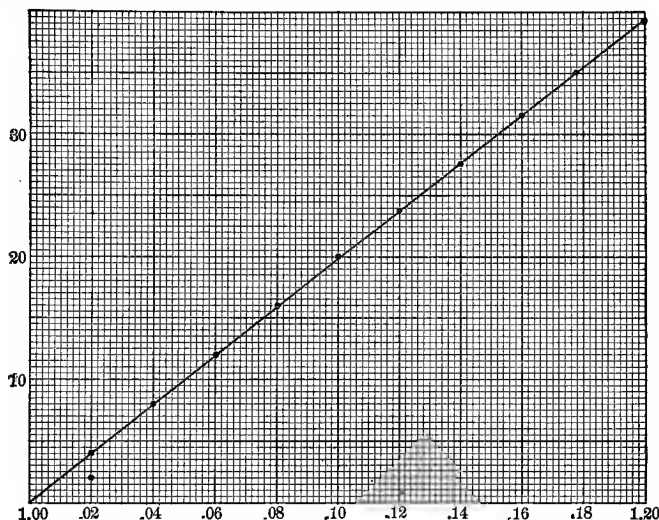


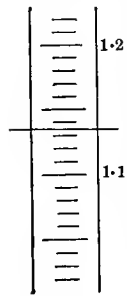
Fig. 52.

The following table gives the values upon which the plot was based. It holds for temperatures of 15°. The content is given in parts by weight of hydrogen chloride present in 100 parts by weight of the solution, *i.e.*, it represents the percentage content of the acid.

Content.	Density.	Content.	Density.
2.14	1.010	21.92	1.110
4.13	1.020	23.82	1.120
6.15	1.030	25.75	1.130
8.16	1.040	27.66	1.140
10.17	1.050	29.57	1.150
12.19	1.060	31.52	1.160
14.17	1.070	33.46	1.170
16.15	1.080	35.39	1.180
18.11	1.090	37.23	1.190
20.01	1.100	39.11	1.200

As regards the measurement of density, this is most readily accomplished with the aid of a hydrometer. This is a glass float, terminating at the top in a narrow tube within which there is a scale. The instrument is made so that it assumes a perpendicular position when placed in a liquid. According to the principle of Archimedes, a body sinks in water until the weight of displaced liquid is equal to the weight of the body. The denser a liquid is, therefore, the less deeply will the instrument sink. The scale in the hydrometer is usually arranged so that the densities are read directly.

**140. Reading scale divisions.**— At this opportunity a few words may not be amiss with regard to the method of reading scale divisions, for this is something that every scientist has to do repeatedly. The divisions on a scale must obviously be some distance apart, and therefore the position to be read does not usually correspond exactly to a scale division, but usually lies between two divisions. Thus it becomes necessary to accustom one's self to estimating fractional distances, and, in fact, it is usual to base such estimations upon the decimal system, reading to tenths. The astronomers, to be sure, who have to make such estimations with great precision, go still farther and learn how to estimate twentieths and even fiftieths.



The diagram shows a vertical scale with horizontal tick marks. A horizontal line is drawn across the scale, representing the surface of a liquid. The line is positioned between two major scale divisions. The upper division is labeled '1.2' and the lower division is labeled '1.1'. The horizontal line is located approximately 40% of the way up from the '1.1' mark, indicating a reading of 1.14.

Fig. 53. Fig. 53 represents a possible scale-reading, the horizontal line across the whole scale representing, let us assume, the place where the surface of a liquid touches the scale of a hydrometer, as is seen when one looks through the liquid. Evidently this line is a little below the middle of the distance between two neighboring scale divisions, but is distinctly more than a quarter of the distance away from the nearer division. The distance from this division, therefore, is less than 0.5 but considerably more than 0.25. One would estimate, in such a case, the reading as 0.4.

Now what is the actual reading? We find below the number 1.10 and above the number 1.20 and halfway between these, a line on the scale that is distinctly longer than the other scale divisions. Evidently each scale division is 0.01 apart from the

next division and the longer lines come every fifth division. For the case shown in the figure, then, the reading would be 1.134.

After a little practice it becomes very easy to make such readings, and it is well for every one to acquire such practice.

### § 19. THE HALOGENS.

**141. Relations of the atomic weights.** — Among the elements occur several groups of which the members show great similarities, not only as regards the properties of the free elements but also in respect to the properties and composition of their compounds. One of the most important of these groups is that of the *halogens*, of which chlorine is the best known and most important member. The whole group consists of the elements:

Fluorine, F = 19.0,
Chlorine, Cl = 35.46,
Bromine, Br = 79.92,
Iodine, I = 126.92,

the symbol and combining weight being written beside the name of each element.

In spite of the differences in the combining weights, the chemical properties of these elements are so similar that almost everything that has been said of chlorine may be repeated of the others. The free elements enter readily into chemical combination, but this property is strongest with fluorine and weakest with iodine. Fluorine is a gas at ordinary temperatures and changes on cooling to a liquid, boiling point  $-187^{\circ}$ . Chlorine is also gaseous at ordinary temperatures; its boiling point lies at  $-33.6^{\circ}$ . Bromine is a liquid, boiling at  $63^{\circ}$ , and iodine a solid which melts at  $114^{\circ}$  and boils at  $184^{\circ}$ . The volatility is, therefore, greatest in the first member of the group and decreases as the combining weight increases. Fluorine is a pale yellowish green, chlorine a somewhat darker shade, bromine a dark red liquid with a deep orange vapor; and finally, iodine vapor is deep violet, while solid or liquid iodine is almost black.

All these elements unite with *hydrogen* in a relation like that in hydrogen chloride, *i.e.*, one combining weight of halogen to one of hydrogen. The hydrogen compounds are all colorless gases, which may be liquefied by cooling, and are soluble in water; they are all acids with their hydrogen replaceable by metals. Of these hydrogen compounds, that of fluorine is the most stable and that of iodine the least so. This is also true of the corresponding salts. The same salts are formed by direct combination of the elements with the metals. The elements are called, for this reason, the *halogens*, or "salt formers." The solubility relations of the salts are similar for the most part, *i.e.*, if chlorine forms a soluble or an insoluble salt with a metal, bromine and iodine will also form similar compounds. Fluorine compounds are likely to differ somewhat in these relations, and fluorine in most respects differs more from the other halogens than they do among themselves.

As to the occurrence of these elements, the first two, fluorine and chlorine, are very plentiful, while the other two are comparatively rare, iodine occurring less frequently than bromine.

It will not be necessary to describe the other halogens in detail, and only those properties will be considered which are distinctly different from those of chlorine.

**142. Fluorine.** — Fluorine is an unusually difficult substance to prepare in the elementary condition, as it reacts chemically with almost everything with which it comes in contact. It has been obtained as a yellowish-colored gas by the electrolysis (p. 155) of its hydrogen compound in a platinum vessel. It reacts instantly with water with evolution of oxygen, undergoing, even in the dark and with great violence, the transformation which, with chlorine, takes place only under the influence of light (p.162). It reacts in the same way with all sorts of hydrogen compounds and on most of the metals, but it forms no oxygen compound. No practical application of this unmanageable element has yet been found.

The hydrogen compound, *hydrogen fluoride* or *hydrofluoric acid*, HF, is in its pure state a colorless liquid, boiling at 19°; it is, therefore, right at the border line between liquids and gases. It

is miscible with water in all proportions, and the more concentrated solutions fume in the air as does the pure acid, for it forms a solution with lowest vapor pressure at a concentration of 48 per cent, boiling at 125° (see p. 167). Hydrogen fluoride and its solutions are dangerous liquids, as they produce ulcerated wounds which heal very slowly.

The fluorine compound most plentiful in nature is calcium fluoride, which crystallizes in cubes and is called *fluor spar*. The most important application of hydrofluoric acid depends on its chemical relations toward silicon, which will be described later.

**143. Bromine.** — Bromine is found associated with chlorine wherever the latter occurs in nature, *e.g.*, in sea water. It may easily be prepared from its compounds by the action of free chlorine: since the chlorine compounds are more stable, these are formed and bromine set free.

This can be seen if chlorine water is added to the solution of a bromide, *e.g.*, to potassium bromide. The liquid is at once colored brownish yellow by the free bromine, the odor of which is just as irritating as that of chlorine and even more unpleasant. If the liquid is now heated, bromine distills off and may be collected.

Free bromine is a commercial article; it is prepared from the mother liquor obtained in the manufacture of potassium chloride, to be described later. It is a heavy liquid (density 3.2), boiling at 60°, and is black, or in very thin layers brownish red, in appearance. It fumes freely at ordinary temperatures and is therefore unpleasant to handle and somewhat dangerous. The vapors have the same poisonous and disinfecting properties as chlorine gas.

Bromine dissolves in water, forming an orange-colored liquid, *bromine water*, which has the properties of the free element, in less active form. If bromine is shaken with magnesium powder it becomes decolorized, due to the combination of the bromine with the magnesium, and the magnesium bromide formed dissolves in water. Free bromine combines with the metals causing an evolution of heat and often a flame, closely resembling chlorine in this respect.

The individual bromine compounds, so far as they are of importance, will be mentioned and described in suitable places.

**144. Iodine.** — Iodine occurs less frequently than bromine. It is found with the latter and with chlorine, particularly in sea water. It is collected and absorbed from the water by various plants and animals (algæ, sponges, etc.), and is therefore found more abundantly in them than in the sea water itself. It is obtained chiefly from the mother liquor of Chili saltpeter (p. 227); the preparation is similar to that of bromine. It may be liberated from its compounds by free bromine as well as by free chlorine. If to a solution of an iodide, *e.g.*, potassium iodide, chlorine water is added drop by drop, the solution is at first colored dark brown because the iodine that is set free dissolves in the excess of iodide. Later, when the iodide is completely decomposed, the iodine separates out and floats on the liquid as a grayish-black precipitate, very slightly soluble in water.<sup>1</sup>

Iodine is also an article of commerce and is obtained in crystalline scales of a violet-black color and slight metallic luster. It dissolves readily in alcohol, forming a brown solution used in medicine under the name "tincture of iodine." It is also soluble, as stated above, in aqueous iodide solutions. The melting point is  $114^{\circ}$  and boiling point  $184^{\circ}$ . Its vapor is very dense and is a beautiful violet. To see this, heat a large, empty flask quite strongly by moving it back and forth over a large flame and then drop in a few small pieces of iodine. This vaporizes instantly and the heavy vapors float and sway like a liquid with the motion of the flask. After cooling, the solid iodine is found in the form of tiny but perfectly formed orthorhombic crystals with brilliant surfaces.

A very striking property of free iodine is the blue coloration which it forms with *starch*. Starch is an organic compound composed of carbon, hydrogen, and oxygen. Its importance lies in the fact that it was the first product known to be formed in the leaves of plants under the influence of light. The starch is stored in the fruits and tubers, so that the kernels of grain, apples, potatoes, etc., consist chiefly of starch. A distinction

<sup>1</sup> An excess of chlorine water will oxidize iodine to colorless iodic acid (*cf.* p. 244).

is made between wheat starch, potato starch, rice starch, etc., according to the source, but all varieties behave in the same way towards iodine.

By boiling with water, starch can be changed to a thick liquid, *starch paste*. If a very thin paste is made (1 : 100) and a little iodine solution added, a dark blue color is produced, due to the combination of iodine and starch. On heating, the solution is decolorized because the compound is decomposed. If the lower half of the test tube containing the "iodide of starch" is placed in cold water, the bottom of the solution becomes blue again with the re-formation of the compound, while the upper half stays colorless until it too has become cool.

By the application of a very dilute iodine solution to slices of potatoes, apples, etc., the presence of starch deposited there in single grains may be shown. The solution necessary for this purpose may be made by rubbing together 1 g. of iodine with 2 g. of potassium iodide and a few drops of water until a dark brown liquid is produced, and then diluting to 400 cubic centimeters.

Just as starch can be detected by iodine, so iodine can be recognized by starch. If to a very dilute potassium iodide solution a little starch paste is added, no coloration results, because this is formed only by *free* iodine. If, however, a trace of chlorine or bromine is added cautiously by means of a stirring rod, the blue color appears at once.

## § 20. SODIUM.

**145. Metallic sodium.** — It has already been mentioned that common salt is a compound of *sodium* with chlorine and that this compound occurs in very large quantities in nature, partly as an aqueous solution in sea water and partly in the solid form as *rock salt*. The way in which the latter is found makes it seem very probable that it is a residue from the natural evaporation of sea water.

At the present time metallic sodium may be obtained in the market at a reasonable price, as it can be made from its compounds electrolytically, just as hydrogen and oxygen are liberated from water by the action of the electric current. Sodium

chloride itself, however, is poorly adapted for this purpose, as it melts at too high a temperature. From a lower melting compound, the hydroxide, the element can be obtained more easily.

Sodium is a *light metal*, *i.e.*, a substance which, although it resembles the more familiar metals in luster, electrical and thermal conductivity, and in certain other properties, differs from them materially in density. The density of sodium is only 0.97; less, therefore, than that of water, while the common metals have densities of 6 and over. Sodium differs from these other metals in its strong tendency to form compounds. In large quantities, therefore, it is kept in air-tight, sealed tin boxes. Smaller amounts may be kept in bottles under *petroleum*. This liquid is a compound of carbon and hydrogen, and sodium does not unite directly with either of these elements.

Since, however, petroleum always dissolves a little atmospheric oxygen, the sodium becomes coated with a gray crust of its oxide, which serves to protect the metal for a long time from further oxidation. When a piece of sodium is removed from the petroleum, it does not look at all metallic; but, as soon as the outer crust is cut away, the soft, silver-white, lustrous metal is seen beneath. The luster lasts only a moment, as the sodium unites at once with the oxygen of the air and becomes covered again with a cloudy film. If a small piece of sodium is left exposed in a shallow dish, it is changed to a liquid in a short time. This is due to the fact that the oxygen compound removes water, for which it has a strong affinity, from the air and dissolves in it.

**146. Caustic soda.** — If a small piece of metallic sodium is thrown into water, the heat evolved from the resulting reaction causes it to melt, and the shining, metallic globule darts back and forth on the surface of the water with a hissing noise and an evolution of a gas. Finally, there remains only a vitreous, glowing drop, which, after a few seconds, is wet by the water and dissolves with a crackling sound. Care must be taken to avoid injury from flying particles.

To determine what gas is formed, pour some water into a dish and place in it an inverted cylinder full of water. Wrap a piece



of sodium, about half as large as a pea, in filter paper, take hold of it with pincers, and skillfully place it under the mouth of the cylinder. The paper serves to keep away the water long enough for its introduction to the desired place. The metal melts, rises quickly in the cylinder, and evolves a gas which partly replaces the water. After the action ceases, close the cylinder with a plate of glass, remove it from the dish of water, and test the gas with a glowing splinter; it proves to be hydrogen.<sup>1</sup>

Sodium, therefore, drives out the hydrogen from water by combining with oxygen; its affinity for the latter is strong enough, even at ordinary temperatures, to effect this decomposition. The resulting product is evidently soluble in water and for that reason cannot be recognized directly. Its presence may be detected, however, by use of suitable reagents.

We know that blue litmus is colored red by acids. If a little litmus solution, colored red by the careful addition of hydrochloric acid, is poured into the liquid in which the compound of sodium has been dissolved, the red liquid immediately turns blue. The test can be made more conveniently if paper colored with the red litmus solution is used. *Red litmus* paper is turned blue as soon as the solution is brought in contact with it.

The compound of sodium that has this effect is called *caustic soda*. It has the property of counteracting the action of acids on litmus paper. We shall see that it also counteracts other actions of acids.

Caustic soda, so called because of its strong caustic action, is found on the market in the form of a white, easily fusible mass which, for convenience in handling, is commonly cast in cylindrical sticks. Caustic soda dissolves in water freely and the solution becomes hot in contrast to the behavior of most solid substances, which use up heat in dissolving and therefore cause a lowering of the temperature of the solution. The aqueous solution of caustic soda has a slippery feeling to the fingers

<sup>1</sup> The gas usually burns with a yellow flame; this is due to the presence of traces of sodium compound in the gas, and all compounds of this metal impart a yellow color to the flame. If the gas is allowed to stand for some time before lighting, until all the fumes have settled, it will then burn with the pale blue flame that is characteristic of hydrogen.

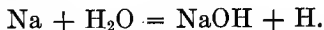
because it dissolves the skin. It must, therefore, be handled carefully. If a little wool or a bit of horn is warmed with caustic soda it will at once disintegrate and dissolve.

**147. Formation of common salt.**—Place a few grams of caustic soda in a shallow dish, add a little litmus solution, some water, and then cautiously a little hydrochloric acid. A strong evolution of heat shows at once that a chemical reaction is taking place. Where the acid is momentarily in excess, the litmus becomes red, but the blue color reappears on stirring. Continue pouring in hydrochloric acid with constant stirring, until suddenly the blue color, which at first keeps coming back, disappears entirely and the characteristic red color, due to the acid, takes its place permanently. Now add caustic soda solution very carefully until a point is found at which the red color just vanishes, and, if the work has been carried out skillfully, the reaction may be stopped at a violet transition stage. The resulting solution does not react acid nor does it show the reaction of caustic soda towards litmus which is known as *basic*. It will not color blue litmus red nor red litmus blue. Such a solution is said to be *neutral*.

To find out what has been formed, the liquid must be evaporated to remove the water. A salt-like residue remains which by its taste and by all its other properties is recognized as table salt. Table salt, also called common salt, is *sodium chloride*. The chlorine of the hydrochloric acid and the sodium of the caustic soda have united, therefore, to form sodium chloride. The hydrogen of the acid and the oxygen of the base, on the other hand, have combined to form water, which, together with the water used in preparing the solution, has been removed by evaporation.

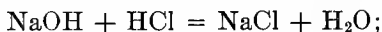
**148. Composition of caustic soda.**—The relations are somewhat complicated by the fact that caustic soda is not a simple oxide of sodium. It is composed of sodium, oxygen, and hydrogen in a relation that is expressed by the symbol  $\text{NaOH}$ , in which Na is the symbol for sodium. The name *sodium hydroxide* indicates the presence of hydrogen. Since the formula of water is  $\text{H}_2\text{O}$ , the action of sodium on water is evidently to drive

out half the hydrogen and to unite with what is left. The equation is, therefore,



The OH group, which occurs frequently in chemical compounds, and which is combined with sodium in sodium hydroxide in the same way that chlorine is combined with sodium in salt, has been given the name *hydroxyl* from syllables in the words *hydrogen* and *oxygen*. Just as a chlorine compound is called a chloride, so a hydroxyl compound is called a *hydroxide*.

Knowing the formula of sodium hydroxide, the chemical reaction between sodium hydroxide and hydrochloric acid, which was just studied experimentally, can now be expressed in symbols,



in words: sodium hydroxide and hydrochloric acid form sodium chloride and water.

**149. Bases.** — Substances like sodium hydroxide, which react with acids in such a way that the acid properties disappear, are called *bases*. This name depends on the fact that they are, for the most part, not easily volatile, whereas many acids are. The old chemists therefore believed them to be the true foundation, or base, of chemical compounds and the acids to be the changeable constituents. Nowadays both substances are assumed to play equally important parts, but the old name is still retained, though no attention is paid to its original significance.

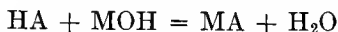
Just as we recognize acids as hydrogen compounds, so we may consider *bases as hydroxyl compounds*. Here also it is true that although all bases are hydroxyl compounds, not all hydroxyl compounds are bases. Water, for instance, is a hydroxyl compound, as the formula HOH indicates. But water is neither acid nor basic, for since it is a compound of hydrogen with hydroxyl, the two unlike components neutralize one another.

Common slaked *lime*, as the mason uses it, is a base, *i.e.*, a hydroxyl compound, namely the hydroxide of *calcium*. If lime is stirred into a little water and a piece of red litmus paper touched with a drop of this solution, a blue spot is at once produced which may be changed back to red by hydrochloric acid. If hy-

drochloric acid is added slowly to a lime paste, the lime dissolves with a strong evolution of heat, and a neutral salt may be made exactly as with sodium hydroxide. The only difference lies in the fact that lime, or calcium hydroxide, is only slightly soluble in water, and, for this reason, the greater part remains in the solid state in contact with a dilute aqueous solution. The resulting calcium chloride, on the contrary, is very soluble in water, so that to obtain it in the solid form the water must be boiled off. If this is done, there remains finally a white salty mass, called *calcium chloride*, which, because of its great affinity for water, we have used in an experiment for drying hydrogen (p. 141).

**150. Formation of salts from bases.** — All metals, generally speaking, can combine with hydroxyl to form bases. Not all of these are soluble in water, and since only the soluble ones can act on red litmus paper, the insoluble bases cannot be detected in this way. All of them, however, react with acids in such a way that the hydroxyl unites with the hydrogen to form water, while the metal combines with that part of the acid which was originally joined to hydrogen. In hydrochloric acid this part is chlorine. We shall soon become acquainted with a large number of elements, as well as combinations of elements, which have hydrogen compounds that are acids.

If such an element, or group of elements, is designated by the symbol A, then HA is the general symbol of an acid. If, on the other hand, M represents a metal, then MOH is the general symbol of a base. When the chemical reaction

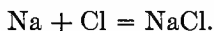


has taken place between an acid and a base, the product MA, formed together with water, is called a *salt*. It will be seen that this name is a generalization of the name "salt" given to sodium chloride; the latter may be formed in the same way, since if Cl is substituted for A and Na for M, the equation shown on page 179 results and is, therefore, only a special case of the general equation.

Since in all reactions of this type the properties of the acids

and bases disappear with the formation of the neutral salt and water, they are usually called *neutralization reactions*.

It may be stated at this point that neutralization reactions are not by any means the only ones by which salts are formed. We have seen, for example, that chlorine can combine directly with the metals. If a small piece of sodium is introduced into a bottle of chlorine, the two elements combine, the reaction taking place rapidly, although not violently enough to produce a flame. The sodium is changed to a white mass found to be common salt. The corresponding chemical equation is



**151. Measuring the strength of acids and bases.** — In neutralizing an acid by the addition of a base, the transition from the acid to the basic reaction takes place with an almost inappreciable excess of substance. Dissolve some common salt in water, divide the solution into two parts, and add a little litmus solution to each. Dip the point of a glass rod into some hydrochloric acid and stir one of the solutions with it; the liquid is suddenly turned red. Repeat the experiment with the other solution, this time dipping the rod into caustic soda solution; on stirring the liquid becomes blue. Both experiments indicate the truth of the law of constant proportions (p. 96), as they show that there is only one single, perfectly definite relation in which acid and base unite to form a neutral salt.

A method for measuring the strength of an acid or a base in a simple way has been based on this reaction. While litmus paper gives *qualitative* proof, *i.e.*, answers the question as to whether a substance of one class or the other is present, the reaction indicated above furnishes the possibility of a *quantitative* determination or measure of the amounts of substance present.

For this purpose, prepare a solution of hydrochloric acid containing in a liter exactly one combining weight in grams, *i.e.*, 36.47 g. (Cl = 35.46, H = 1.01). Such a solution may be prepared in several ways. One of the simplest methods is based on the knowledge of the density of such a solution. This is 1.0172

at 15°, so that if a solution of pure hydrochloric acid in water is made up to this density, it will contain the required amount of hydrogen chloride per liter.

Similarly, the combining weight of sodium hydroxide (Na = 23.00, O = 16.00, H = 1.01) is 40.01. If, therefore, 40.01 g. of pure sodium hydroxide are weighed out and dissolved in a "liter flask," *i.e.*, a flask on the neck of which the volume of one liter is indicated by a line, on diluting up to the mark a solution is obtained which will exactly neutralize an equal volume of the hydrochloric acid solution. Commercial sodium hydroxide is not pure but always contains more or less water. It is, therefore, best to weigh out somewhat more, perhaps 42 g., of hydroxide, dissolve it and then determine the strength of the solution.

For purposes of measuring volumes the chemist uses two simple instruments, *burettes* and *pipettes*. The names are derived from the French, as these methods of analysis were introduced by the French chemist Gay-Lussac. A burette is a glass tube graduated in centimeters and tenths, and is closed by a stopcock at the lower end. This cock may be of glass, or, in the simpler form, is a short piece of rubber tubing, closed by a pinchcock on the outside of the tubing, or by a small glass ball within it. In order that the flow may be more uniform, a small glass tip is fixed below the valve (see Fig. 54). By pressing the ends of the pinchcock gently, the liquid can be delivered from the burette in regulated amounts. Fill such a burette with some of the hydrochloric acid solution containing 36.45 g. per liter, known as a *normal* solution, and let some of the acid run out, so as to leave the tip of the burette filled with acid and also to leave the upper level of the liquid at the uppermost mark on the burette (Fig. 55). The apparatus is then ready for use.

The pipette (Fig. 56) is a glass tube with a central enlargement, which, when filled to a mark on the upper stem, contains a definite volume of liquid, *e.g.* 20 cc. This volume is marked on the pipette. Fill such a pipette by dipping the lower end of the tube into the sodium hydroxide solution and sucking until the liquid has risen somewhat above the mark. Then remove the

pipette from the mouth and at the same time close the upper opening with the index finger. Place the point of the pipette against the side of the vessel containing the solution, and very carefully let the liquid run out until the upper level just touches the mark. Now transfer the pipette to a dish and allow all the caustic soda solution to run out, touching the point of the pipette against the side of the vessel at the last; in this way exactly 20 cc. will be delivered.

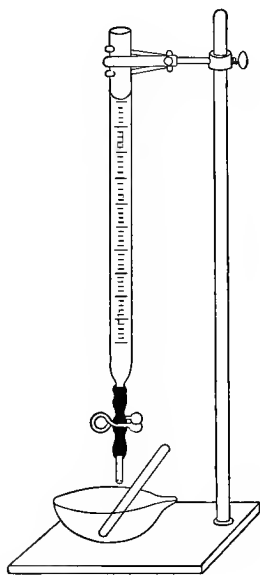


Fig. 54.



Fig. 55.



Fig. 56.

Now add a few drops of litmus solution and run in hydrochloric acid from the burette. At first the solution stays blue, but later red spots are formed which disappear quickly on stirring. From this point add the acid more and more cautiously until the red spots fade very slowly. Now introduce the acid drop by drop, until finally the amount of acid required to neutralize the alkali is known to a single drop.

Obviously this experiment is the same as that already described on page 178, except that instead of using indefinite amounts accurately measured volumes were taken in order to determine the exact volume relations. Assume that we have used 20.65 cc. of normal hydrochloric acid to neutralize 20 cc. of the caustic soda solution; we must conclude that somewhat more than one combining weight of caustic soda is present in a liter, or, more definitely speaking, the solution is  $\frac{20.65}{20.00}$  as strong as it was intended to be. A liter contains, therefore, not 40.01 g. sodium hydroxide but  $\frac{40.01 \times 20.65}{20.00} = 41.31$  g.

If it is desired to make the hydroxide solution exactly normal, it must be diluted in the proportion 20.00 : 20.65. Since 980 cc. are left, the volume must be brought to  $\frac{980 \times 20.65}{20.00} = 1011.85$  cc., *i.e.*, 31.85 cc. of water are to be added. This can be added accurately from a burette, and after the solution is thoroughly mixed it will be found to be exactly normal.

By means of these two solutions the strength of any soluble acid or base can be determined if its combining weight is known; for each cubic centimeter used corresponds to  $\frac{1}{1000}$  of the combining weight in grams of the substance to be analyzed. If  $C$  represents the combining weight and  $n$  the number of cubic centimeters used, the amount of substance in grams is  $\frac{nC}{1000}$  g. Such rapid methods, called *titration*, from the French *titre*, are used constantly in chemical work, and are so simple that such analyses may be carried out with great accuracy by half-grown boys.

#### § 21. POTASSIUM.

**152. Potassium.** — Another light metal, very similar to sodium but occurring less abundantly, is *potassium*. It may, like sodium, be prepared by electrolysis, and has almost the same properties as sodium. Its density is 0.86, even less than sodium, and its tendency to combine with oxygen is greater. If a small piece of potassium is thrown into water, the heat of reaction is so great



that the hydrogen takes fire as it is liberated and burns with a violet flame. Potassium compounds color the flame reddish violet, just as sodium compounds color it yellow and can be distinguished in this way.

The action of potassium on water is like that of sodium. One combining weight of hydrogen is liberated and potassium hydroxide, KOH, is formed. This, too, is a readily soluble base; its aqueous solution colors litmus blue, has a soapy taste, and neutralizes acids. In the pure state potassium hydroxide, often called *caustic potash*, looks exactly like caustic soda. It is usually cast in sticks, and dissolves freely in water with a strong evolution of heat. The solution can scarcely be distinguished from caustic soda solutions by its behavior, and all the reactions of sodium hydroxide may be duplicated by it. This is because of the presence of the common constituent, *hydroxyl*, OH, to which the basic properties are due.

The combining weight of potassium is 39.10, that of potassium hydroxide 56.11. If about 60 g. of the hydroxide (60 g. are taken because the commercial article is not pure) are dissolved in a liter of water, an approximately normal solution is obtained, *i.e.*, one which will neutralize an equal volume of *normal* hydrochloric acid. It can be made exactly normal in the way described on page 184. Acids may be titrated with it, as with the sodium hydroxide solution, and it can be shown that *a given amount of any acid solution requires equal volumes of the two normal alkali solutions for its neutralization*. This is a simple confirmation of the law of combining weights.

**153. Salts of potassium.** — Neutralize a few grams of potassium hydroxide with hydrochloric acid and evaporate the solution to obtain the salt formed; it is a white crystalline substance in appearance similar to sodium chloride. It also crystallizes in the isometric system, but differs materially from common salt in being distinctly more soluble in hot water than in cold. Dissolve as much of the salt as possible in boiling water, stopper the flask to prevent evaporation, and let the clear liquid cool. A considerable quantity of solid salt will separate out. The solubility is about twice as great at the boiling point as at 0°.

Potassium compounds occur in many minerals; thus feldspar (orthoclase) is a common potassium compound. All cultivated lands contain soluble potassium compounds which are taken up by plants, for the proper nourishment of which it is absolutely essential. Certain plants, as for example tobacco, grapes, and beets, need so much potassium salts that it is necessary to add the latter artificially to the soil in order to obtain the best yield. Large deposits of potassium chloride, and some compounds formed with it, occur in Germany, and these salts are mined and shipped all over the world to be used in fertilizers, as similar potassium deposits have not been found elsewhere. In the natural state potassium chloride forms regular, transparent, cube-like forms which in the pure state are colorless but are occasionally colored blue or otherwise by some foreign element. The mineral name is *sylin*.

**154. Isometric system of crystals.** — Such regular shapes, which are formed independently when a substance passes into the solid state, are called *crystals* (p. 31). We have already seen that crystals of the same substance can differ markedly in shape and size but that their corresponding bounding surfaces are always inclined to each other at the same angles. Moreover, they are governed by other, very definite laws which depend on their *symmetry relations*, i.e., upon the manner in which corresponding forms are repeated.

Take a cube, for instance; this is the form in which potassium chloride (and also sodium chloride) most frequently crystallizes. A wooden or pasteboard model will serve as well as the natural crystal. Hold the cube between two points which lie in the centers of two opposite surfaces, and revolve it about this axis; after passing through an angle of  $90^\circ$ , the cube will again be in a geometrical position exactly like that at the start. Such a rotation by which a body comes into geometric coincidence with itself may be called a *movement of superposition*. In a cube, therefore, a rotation through  $90^\circ$  causes superposition. During a complete revolution of  $360^\circ$  the cube comes into such a position four times. The axis about which it revolves is known as an *axis of symmetry*, and in this case it is a *quaternary sym-*

metry-axis, since four superpositions occur in a complete revolution about it.

Fig. 57 shows a cube, as seen from above, which is so placed that the axis of symmetry is perpendicular to the plane of the paper and is represented by a point. Every rotation through  $90^\circ$  obviously causes superposition.

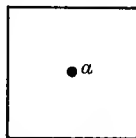


Fig. 57.

If the middle points of two other opposite faces are selected as the ends of an axis of rotation, exactly the same relations hold and this second position of the cube cannot be distinguished from the first. The same is true of the third pair of opposite sides and its corresponding axis of symmetry. Hence, these three axes are equivalent.

The cube, therefore, is a solid body having three equivalent quaternary axes of symmetry. It is not by any means the only figure of this type, for a regular octahedron has exactly the same properties. In the latter case the three quaternary axes of symmetry connect opposite corners, and the student should convince himself by holding an octahedron in this way that it actually has three equivalent axes. Fig. 58 shows an octahedron as looked at from above. Besides the cube and the octahedron, there are numerous other forms with the same symmetry relations.

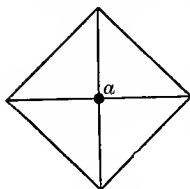


Fig. 58.

In addition to the three quaternary axes, all of the forms have four *ternary axes of symmetry*. In a cube they connect opposite corners in which three surfaces cut each other at the same angle. In this case a revolution of  $120^\circ$  takes place before the cube is again coincident. This means that there are but three coincident positions and that the axis is a ternary one. As the cube has eight corners, there are four such axes connecting opposite corners, making, therefore, four ternary axes. These axes also are equivalent.

It can easily be shown, moreover, that this is true of the octahedron, in which case the axes connect the centers of oppo-

site faces. Fig. 59 shows the two forms seen from above and with the ternary axis perpendicular to the paper.

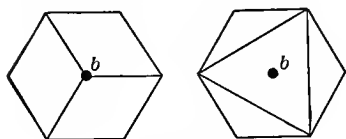


Fig. 59.

Finally there are six *binary axes*, which in a cube connect the centers of opposite edges. In the octahedron they are also present and connect the middle points of opposite edges. A revolution of  $180^\circ$  is required

with a binary axis to cause coincidence.

Fig. 60 shows the two forms, cube and octahedron, with the binary axes of symmetry perpendicular to the plane of the paper. The other shapes mentioned above, which have three

quaternary axes of symmetry, also show the other symmetry relations. They make, therefore, a family of related forms, or, as it is called, a *crystal system*. A natural law has been discovered

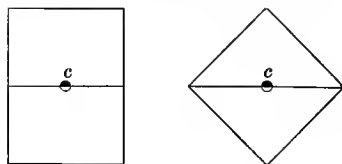


Fig. 60.

which states that *all the crystal forms which can be formed side by side from a given substance belong to the same family*. Thus, for example, besides the cubes of potassium chloride, it is possible to find in the crystals of this salt the faces of the octahedron and many other faces, but only those faces which correspond to the definite symmetry relations that have just been described and no others.

This family of forms is called the *isometric* or *regular system*; thus it may be said that sodium chloride and potassium chloride crystallize in the isometric system. Later on we shall become acquainted with substances that crystallize in five other systems, — *tetragonal*, *orthorhombic*, *hexagonal*, *monoclinic*, and *triclinic*. Each of these systems is characterized by special symmetry relations.

## § 22. MAGNESIUM.

**155. Magnesium**, like sodium and potassium, is a light metal, but differs from them in not being appreciably oxidized in the air; it can be kept, therefore, without special precautions. It is a white metal somewhat like zinc in hardness and other physical properties; it melts at a fairly high temperature and may be cut, filed, or drilled.

Like sodium, it can be obtained by *electrolysis, i.e.*, by decomposing suitable compounds with the electric current. For this purpose magnesium chloride is used. This salt melts fairly readily and on passage of the current gives chlorine at one electrode and metallic magnesium at the other.

Metallic magnesium does not occur in nature but its compounds are widely distributed. Dolomite, a mineral of which great mountain ranges are formed, is a magnesium compound. Likewise, sea water contains magnesium chloride, though much less of it than of sodium chloride.

The most striking property of magnesium is its exceedingly *brilliant* combustion. A ribbon of magnesium may be lighted and will burn with a dazzling white flame, whereby a great deal of light is furnished. If magnesium powder is blown into a flame, such a bright flash results that photographs can be taken by means of it. Other magnesium "flash lights" are made by mixing the powdered metal with substances rich in oxygen and setting fire to the mixture. These powders are somewhat dangerous to handle.

The chemical process that results hereby is a simple *oxidation*; the *magnesium burns to magnesium oxide*. The latter is a solid, infusible even at white heat, and thus, as the heat of combustion is great, the "flash" is caused by the oxide being heated to a very high temperature. The oxide is also called *magnesia* and is a white powder which was known long before the metal. It is sold on the market as *calcined magnesia* and finds application in medicine. In contrast to sodium, magnesium does not react with water at ordinary temperatures, and it is only when powdered magnesium is boiled in water that the slightest evolution of hydrogen takes place. The heated metal

will, however, decompose water vapor and is thereby transformed into the oxide.

**156. Magnesium chloride.** — If magnesium is treated with hydrochloric acid, a violent evolution of hydrogen results. This, as we have already learned, is due to the displacement of the hydrogen of the acid by the metal. A colorless solution is obtained, usually containing a few black spots due to impurities in the magnesium. Filtration gives a perfectly clear solution. It is a rather difficult matter to get crystals by evaporating the solution, for the magnesium chloride is so extremely soluble in water that the solution must be evaporated to a very small bulk before crystallization begins.

The salt obtained in this way, *magnesium chloride*, consists not merely of the two elements but contains water as well. The water escapes as a vapor when the substance is gently heated. In many other cases it also happens that salts as they crystallize from an aqueous solution, whether by cooling or by evaporation, combine with a part of the water. This water is known as *water of crystallization*, since it is not an essential constituent of the salt and yet determines the form in which it crystallizes. In most cases it may be removed by heat, leaving the anhydrous salt. In the case of magnesium the compound is  $MgCl_2$  and differs from the alkali chlorides in containing two combining weights of chlorine to one combining weight of the metal. Magnesium, therefore, is called a *bivalent* metal on the basis of the following considerations.

**157. Valence.** — Chlorine combines with hydrogen in one proportion only, namely in the ratio of the two combining weights. If hydrogen is selected as the standard for measuring the *capacity for combination*, called the *valence*, and its combining power toward other elements is taken as unity, then the combining power of chlorine must be equal likewise to unity, because one combining weight of chlorine combines with just one combining weight of hydrogen; chlorine, therefore, is called *univalent*. In the same way, sodium and potassium are each univalent, since each combines with one combining weight of chlorine. Oxygen, on the other hand, is *bivalent*, because it unites with two combining weights

of the univalent hydrogen. When, however, bivalent magnesium unites with bivalent oxygen it is to be expected that one combining weight of each element is necessary and sufficient to form a saturated compound; and, as a matter of fact, magnesium oxide has the composition represented by the symbol  $MgO$ .

From this the rule is derived that *the elements combine with one another in such a way that an equal number of valences are opposed to one another*. Then, if the elements have different valences, the number of combining weights of each must be inversely proportional to the respective valences. Thus if the valences are known, it is very easy to remember the composition and symbols of the different compounds.

It must be at once stated, however, that all compounds do not follow this simple rule. The most important ones do, however, and it is better to learn the exceptions than to give up the valence rule entirely.

To make the application of the rule simpler, the symbol of each element is often written with as many dashes, or bonds, as it has valences. All compounds which follow the rule can then be written in such a way that the bonds of the combining elements run together and no free bonds are left. Hydrogen is thus written  $H -$  and chlorine  $Cl -$ . In the formula  $H - Cl$  the two bonds join and the rule is followed. Oxygen must have two bonds, as it is bivalent. Water will then be written

$O \begin{array}{l} / H \\ \backslash H \end{array}$ , in which oxygen has two bonds and each hydrogen one.

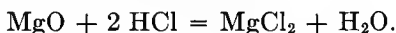
Magnesium oxide is written  $Mg = O$ , as magnesium and oxygen must each have two bonds.

To get a rough conception of the matter, we may imagine that each atom has as many hooks as it has valences. In normal or *saturated* compounds, the atoms are hung together in such a way that all the hooks are joined and that none are useless.

**158. Carnallite.** — Crystallized magnesium chloride has the composition  $MgCl_2 + 6 H_2O$ , *i.e.*, it contains six combining weights of water of crystallization. It occurs in this form in the Stassfurt salt deposits which are the source of the potassium compounds. It also combines with potassium chloride to form a

double salt of the composition  $\text{KCl} \cdot \text{MgCl}_2 + 6 \text{H}_2\text{O}$  known as carnallite, the chief potassium mineral in the Stassfurt deposits. Such double salts are formed by crystallization from the mixed solutions of the single salts, and thus carnallite can be obtained by evaporating mixed solutions of potassium chloride and magnesium chloride. On mixing the solutions there is no special evidence of the formation of a compound, but this formation is only noticed when crystals form. Potassium chloride alone will separate from a hot solution and magnesium chloride will stay back in the mother liquor. From a cold solution both crystallize together as carnallite.

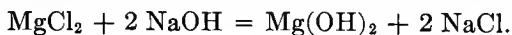
**159. Oxides and hydroxides.** — Magnesium chloride can also be obtained by dissolving magnesium oxide, instead of the metal, in hydrochloric acid. The equation is



This is similar to the equation which represents the combination of hydrochloric acid with caustic soda, except that in this case there is no true base present but an *oxide* which contains no hydrogen and therefore no hydroxyl group. The base derived from magnesium must contain hydroxyl and, as magnesium is bivalent, it needs two hydroxyl groups.

Definite valence numbers can be given not only to elements but also to groups of elements, of which the hydroxyl group is an example. Hydroxyl is left when one hydrogen is removed from water. This leaves one free valence, and the OH group is, therefore, univalent. This can be shown by drawing the bonds: of the two oxygen bonds only one is joined to hydrogen, the other is free:  $-\text{O}-\text{H}$ . Therefore, if magnesium hydroxide exists it must have the composition  $\text{Mg}(\text{OH})_2$ , where the subscript 2 refers to the whole contents of the bracket.

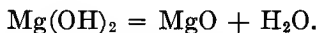
Magnesium hydroxide is obtained by decomposing magnesium chloride with sodium hydroxide or with potassium hydroxide. The aqueous solution of the chloride on being mixed with the soluble base gives a white, somewhat gelatinous and not at all crystalline precipitate, formed according to the equation





This equation is an example of *metathesis*, or, in other words, of a mutual exchange of components. Reactions of this type frequently occur between solutions of salts and salt-like compounds which have a "paired" composition. There is, furthermore, a rule which states that of the possible combinations those will be formed which under the existing conditions are *least soluble*. Now of the four substances in the above equation, three, magnesium chloride, sodium chloride, and sodium hydroxide, are all readily soluble, while magnesium hydroxide dissolves but slightly. It is formed for this reason and is deposited as a white precipitate which can easily be purified by filtering and washing.

A simple relation exists between magnesium oxide and hydroxide, as they differ only by the elements of water. The equation can be written



This equation expresses a chemical reaction which may take place in either direction. If magnesium hydroxide is heated, it decomposes into the oxide and water vapor; and, if magnesium oxide stands in contact with water, it combines with it to form magnesium hydroxide. The two substances look much alike (both are white powders without any visible crystalline properties), so that other methods must be used to distinguish them. The use of the *balance* is the best method. Magnesium oxide can be bought on the market under the name of *magnesia usta*, or calcined magnesia. Heat a little of this gently in a weighed porcelain crucible, cool, weigh and determine the weight of oxide by difference. Then pour a little water into the crucible and remove the excess by heating at a temperature slightly above 100°. To prevent superheating, support the crucible containing the moist powder inside a second crucible in such a way as to allow an air space between, and then heat the outer crucible with a small flame. Such an arrangement of the crucible is known as an *air bath*. After the excess of water has evaporated completely, allow the inner crucible to cool and again weigh it. It will be found decidedly heavier. If the weight of the hydroxide is now divided by the weight of the oxide and the quotient

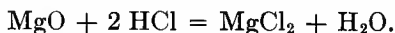
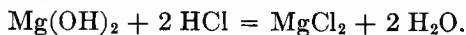
multiplied by 100 the percentage gain in weight is found. Just what this should amount to, if the experiment were carried out without an error, can be calculated from the combining weights.

$$\text{Mg} = 24.32, \text{O} = 16.00, \text{H} = 1.01.$$

Therefore,  $\text{MgO} = 40.32$  and  $\text{Mg(OH)}_2 = 58.34$ . If, then, the latter weight is divided by the former and multiplied by 100, the result is 144.7. 100 parts of magnesium oxide, therefore, must give rise to 144.7 parts of magnesium hydroxide. The deviation of the observed values from the theory represents the sum of the experimental errors, which are due partly to the greater or less purity of the preparation and partly to errors in the experimental work. By repeating the experiment several times, an idea of the source and amounts of these errors can be obtained.

A substance formed from another by the removal of water is called an *anhydride*. Magnesium oxide, then, is the anhydride of magnesium hydroxide.

Salts are formed by the action of acids on the oxide, as well as by their action on the hydroxide, except that in the first case the amount of water formed is only half as great. For example the two following reactions take place with hydrochloric acid:



The ease with which anhydrides form differs materially in different cases. It is very difficult, for instance, to prepare sodium oxide, the anhydride of caustic soda, since on being heated strongly the latter vaporizes without decomposing and does not lose water.

## CHAPTER VII.

### SULPHUR AND THE ALKALINE EARTH METALS.

#### § 23. SULPHUR.

**160. Native sulphur.** — Because of its striking properties and frequent occurrence, sulphur belongs to the oldest-known substances and even the alchemists of the Middle Ages classed it as one of their elements. When, in more recent times, the modern conception of an element as a substance which could not be decomposed into simpler components was developed, it was soon determined that sulphur was also an element according to this view.

Sulphur occurs most frequently in Nature in localities where there is, or has been, volcanic activity, but it is also formed by the action of vegetable substances on sulphur compounds. Natural sulphur is generally impure, and it has already been shown that it may be purified by melting (p. 44) and by distillation (p. 65). The pure varieties of sulphur occur for the most part in the shape of crystals of the orthorhombic type. The type occurring most frequently is an elongated octahedron which has the property that all sections that can be laid through any four edges in the same plane are rhombic; these are all perpendicular to one another and are all different. For this reason the octahedron has the following geometric properties.

**161. Orthorhombic crystals.** — If two opposite corners of the orthorhombic octahedron are joined by an axis, about which the octahedron is rotated, it must be revolved through  $180^\circ$  in order to come into superposition. For at right angles to each of the three axes is a rhombic section, and an attempt to bring a rhombus into superposition by revolving it in its own plane around its center shows at once that a revolution of  $180^\circ$  is necessary. Moreover, the axes are of different lengths and are, therefore, not equivalent.

The orthorhombic system, in which sulphur crystallizes, has, like the isometric system (p. 186), three symmetry axes perpendicular to each other. The difference is that the axes are all of different lengths and are not quaternary but binary. Furthermore, since there are no axes of symmetry other than the above-mentioned ones, it is evident that the orthorhombic system is far less symmetrical than the isometric system. Fig. 61

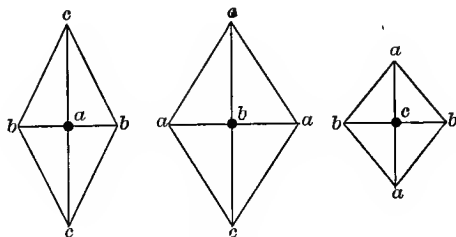


Fig. 61.

shows the sections that can be made perpendicular to the three axes. Now there is the law governing all crystals (p. 188) that in addition to the simplest boundary surfaces other faces may form on a crystal but that all such faces must show the same geometrical relations with reference to motions of superposition. On native sulphur, for example, faces are often found on the edges and corners of the octahedron, but there are always several such faces (two or four) and they are so placed that they change places after the crystal has been rotated  $180^\circ$  on one of the three axes of symmetry. And so, no matter how complicated a form sulphur may have, it is always so shaped that by revolving it through  $180^\circ$  about any one of its three axes it will again come into a position of superposition.

**162. Properties of sulphur.** — The density of sulphur is not great but is almost twice that of water. Its hardness is also slight. It does not conduct electricity but on the contrary is so good an insulator that in earlier times electrical machines were built with sulphur terminals. Its luster is greasy. Pure crystals are translucent and yellow, but most crystals appear opaque, because, like loaf sugar, they are composed of countless

small, irregularly placed crystals which do not permit the unbroken passage of light.

Sulphur melts at  $120^{\circ}$  to a honey-yellow, mobile liquid which hardens quickly on cooling. Small objects can easily be made from sulphur and it is therefore much used in making casts of cut stones, etc. It cannot be used in making metal casts, as it combines with the metals chemically and discolors their surfaces.

**163. Behavior on heating.**—If molten sulphur is heated it soon loses its mobility and, with increasing temperature, finally becomes so viscous that the containing vessel may be inverted without spilling its contents. This depends on the fact that the readily liquefied sulphur changes, with absorption of heat, into another viscous form, just as ice is changed into water by heating. The color grows darker at the same time, so that one is reminded of the darkening and carbonizing of wood and other plant substances. Obviously such a change cannot take place with sulphur, for it is an element and cannot be decomposed in any way. If the tough, dark sulphur is allowed to cool somewhat, it changes back again into the other light-colored, mobile form without having undergone any permanent change.

If, however, the viscous sulphur is poured into cold water it retains its plastic properties even after it is cold. In other words the sulphur does not find time during sudden cooling to revert to the form that melts to a mobile liquid and the transformation takes place very slowly at low temperatures. If the plastic sulphur is put aside for a few days, it will be found at the end of that time as a light-yellow, brittle mass, which is in all respects like the ordinary solid sulphur and on heating melts to the light-colored liquid sulphur.

If the viscous sulphur, instead of being cooled, is heated still hotter, it finally changes into a dark brown vapor,<sup>1</sup> which can be condensed, according to the temperature, to solid or liquid sulphur. A fairly high temperature is needed for this vaporization, as sulphur boils at  $445.5^{\circ}$  under atmospheric pressure. Sulphur behaves much like water, inasmuch as it exists in the

<sup>1</sup> The vapors when pure are nearly colorless at the boiling point, but become darker as the temperatures is raised.

solid, liquid, or vapor form according to the temperature. It has been stated previously that all substances behave in this way, although the necessary temperatures are not always so easily reached.

**164. Polymorphism.** — That molten sulphur crystallizes on cooling has already been shown (p. 31). If the experiment is carried out with large masses, well-developed crystals result which, however, do not have the orthorhombic shape of native sulphur crystals but appear as prisms of rectangular cross section with acute end faces. If an attempt is made to cause superposition to take place by rotation about any of the axes, it will be found that a revolution about one axis only, namely the one parallel to the sloping end faces, results in a superposition.

In all other cases coincidence is obtained only after a revolution of  $360^\circ$ . These crystals, therefore, belong to another crystal system which is characterized by a single binary axis of revolution. This is called the *monoclinic system*. Fig. 62 gives an illustration of the simplest form, as seen directly perpendicular to the axis of symmetry.

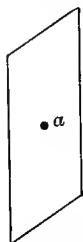


Fig. 62.

It follows from the above that sulphur can exist in two crystalline modifications according to the conditions. If the dark yellow, transparent, and somewhat elastic crystals are kept a few days, their appearance changes; they become opaque and brittle and a careful density determination shows that the density has increased. Monoclinic crystals have the density 1.96, while orthorhombic forms have the density 2.07. Sulphur, then, has not simply one solid form but at least two.

These two forms bear the same relation to each other as do water and ice; for the orthorhombic crystals are more stable at low temperatures and the monoclinic crystals at higher ones. The transition point lies at  $95^\circ$ . Above this temperature orthorhombic sulphur changes into monoclinic sulphur, just as ice changes into water at  $0^\circ$ ; below  $95^\circ$  monoclinic sulphur changes into rhombic sulphur, just as water changes into ice at  $0^\circ$ . The only difference is that the change takes place more

slowly with sulphur than the change of water into ice or of ice into water. Yet the monoclinic sulphur is comparable to super-cooled water, although, unlike sulphur, it is not possible to keep water for several days at a temperature  $75^{\circ}$  below the transformation point.

This fact, that the same substance exists in different crystal forms depending on the temperature, is known as *polymorphism*. The name *allotropy* or *allotropism* has also been used for this phenomenon when it occurs in *elements*, but as there is no reason for retaining the latter name, the word *polymorphism* will be used in this book. If *two* forms exist, one speaks of *dimorphism*. Sulphur is not by any means the only substance or the only element having polymorphic forms. In fact the phenomenon is so common that there are more substances with polymorphic forms than without. Several polymorphic elements will be studied later.

Since this subject deals with differences in crystal form, it follows that polymorphism occurs only in solid substances. In addition to the different crystal forms there often exist amorphous forms of the same substance, as *plastic sulphur* illustrates (p. 197). This, too, changes spontaneously into rhombic sulphur at room temperature. For this reason sulphur is found in Nature only in the form of orthorhombic crystals, because the other forms have had time to change over into the most stable form.

The list of different forms of sulphur is by no means exhausted for there are still other types of sulphur crystals. These are all unstable forms, however, which are formed only under special conditions and soon change into rhombic sulphur, so that it is not worth while to describe them in detail here.

**165. Sulphur dioxide.** — In all these experiments sulphur shows a strong tendency to take fire and burn with a blue flame. The sulphur disappears completely, leaving neither a solid nor a liquid residue. That something new is formed, is shown by the strong odor that is so noticeable when sulphur burns. A gaseous combustion product is formed from sulphur, and its characteristic smell distinguishes it from the products of combustion of hydrogen or of vegetable substances. Then, too, when

sulphur was burned in oxygen (p. 122) no visible combustion product was noticed, but the presence of an acid was indicated when the gas was brought into water.

If the combustion experiment is repeated, the flask carefully stoppered and allowed to cool, it is found that after cooling the pressure in the flask is practically unchanged, if pains have been taken to have the flask perfectly dry inside. The stopper can be removed without having a violent escape of gas from the inside of the flask or a strong suction of air from the outside. From this fact the conclusion may be drawn that the gaseous combustion product of sulphur has approximately the same volume as the oxygen from which it is made. Exact measurements have shown that this is really the case. The new gas is not called sulphur oxide, but as is indicated by its symbol,  $\text{SO}_2$ , is known as *sulphur dioxide*.

If some water is shaken in a flask containing sulphur dioxide, a decrease in pressure is noticed: sulphur dioxide is very soluble in water. The aqueous solution has the same suffocating odor as the gas, and litmus paper shows that it has an acid reaction. As we have learned that all acids contain hydrogen, and since there is none in sulphur dioxide, it must come from the water. This is indeed the case: sulphur dioxide combines with water according to the equation  $\text{SO}_2 + \text{H}_2\text{O} = \text{H}_2\text{SO}_3$ . The resulting acid is known as *sulphurous acid*.

Sulphur dioxide is a colorless gas. It is fairly easily liquefied; the liquid boils at  $-10^\circ$  under atmospheric pressure, and at  $+20^\circ$  it has a vapor pressure of only 3.24 atmospheres. The gas dissolves freely in water, about 50 volumes of gas to one of water. The solution is found on the market under the name *sulphurous acid*, smells strongly of the gas, and loses the dioxide completely on boiling.

**166. Sulphurous acid.** — The aqueous solution of sulphur dioxide soon takes up oxygen from the air and is changed to *sulphuric acid*. It can also take oxygen from numerous other compounds, so that it is used as a *reducing agent*, *i.e.*, as an oxygen remover. Sulphurous acid acts vigorously on plants, killing the green leaves almost at once. In large factory towns the air always contains appreciable amounts of sulphur dioxide from the burning of soft coal



(which usually contains sulphur compounds). The trees in the vicinity are injured and stone buildings are often strongly attacked by the sulphuric acid formed. Even the small amount of sulphur dioxide formed in imperfectly purified illuminating gas is often enough to kill the plants in rooms where this gas is regularly used. Associated with this effect is the power of sulphurous acid to destroy mould and other of the lower plant organisms that are injurious in many processes, and it is for this reason frequently used where beer and wine are made. It also has a bleaching action on vegetable pigments. Place a few colored flowers under a bell jar (a large plain beaker will serve) and burn a piece of sulphur in the jar; soon the flowers will turn white. This property is made use of in bleaching silk, wool, straw, and other materials that would be injured or destroyed by chlorine.

Sulphurous acid forms salts. It differs from the acids previously considered in containing two combining weights of hydrogen, both of which can be replaced by sodium and other metals. The sodium salt is used in photography. It is obtained in large crystals containing seven combining weights of water,  $\text{Na}_2\text{SO}_3 \cdot 7 \text{H}_2\text{O}$ .

**167. Sulphur trioxide.**—Sulphur dioxide, formed by the burning of sulphur in air or in oxygen, is not the only oxygen compound of sulphur. In addition there is a *trioxide* containing three combining weights of oxygen to one of sulphur. It is formed in very small amounts when sulphur burns and is the cause of the white fumes usually noticed during the combustion. Its amount is so small that it cannot be prepared advantageously in this way, although by the burning of sulphur dioxide to trioxide more heat would be liberated.

This is an illustration of *chemical inertia*, where two substances which might combine do not unite at all, or combine but slowly. This phenomenon is shown, too, by detonating gas at ordinary temperatures; with sulphur dioxide and oxygen this inertia exists at higher temperatures. Just as hydrogen and oxygen could be made to combine by bringing the mixture into contact with platinum sponge, so sulphur dioxide can be burned to sulphur trioxide by using platinum sponge at a high temperature.

Moisten a strip of asbestos with a few drops of a platinum solution and then ignite it. Place the platinized asbestos in a tube of about 1.5 cm. diameter which is clamped in an inclined position and arranged so that the asbestos can be heated by means of a burner beneath. The lower end of the tube should be provided with a funnel-shaped enlargement, or an asbestos funnel may be fastened to the end of the tube (Fig. 63).

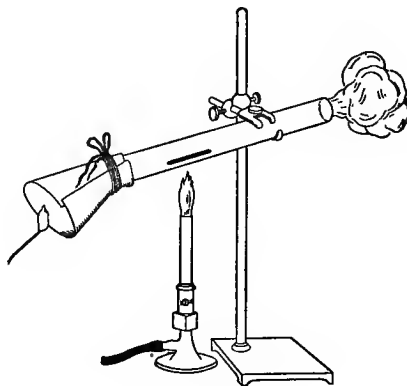


Fig. 63.

Light a small piece of burning sulphur and place it below the funnel so that a mixture of sulphur dioxide and air is drawn over the hot asbestos; the sulphur dioxide is partly converted into the trioxide, which escapes at the top of the tube as white fumes. Condense a little of the vapor by bringing a wet rod in contact with the fumes and then touch the rod to litmus paper and also dip it into a solution of a soluble barium salt: the liquid on the rod has an acid reaction and precipitates barium salts.

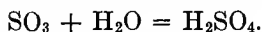
The formation of sulphur trioxide can be expressed by the simple equation



Sulphur trioxide is now prepared on a commercial scale in precisely this way. Other substances may be used in place of

the platinum, particularly ferric oxide, which has a similar effect of hastening the oxidation of the sulphur dioxide. A colorless liquid forms, which soon hardens to a crystalline mass of long white fibers that look much like cotton batting.

The most striking property of sulphur trioxide is its strong tendency to combine with water. When thrown into water it hisses like hot iron. It absorbs water from the air with such energy that it can be kept unchanged only by sealing it up in the containing vessel, completely out of contact with the air. When exposed to the air it fumes freely, the vapor combining with water vapor to form a very slightly volatile compound. This is the cause of the dense white fumes which come from solid sulphur trioxide. The reaction may be written



The new compound,  $\text{H}_2\text{SO}_4$ , is called *sulphuric acid* and is one of the most important substances in the whole chemical industry. As a general chemical tool it plays much the same part that iron does in the world of machinery.

**168. Sulphuric acid.** — Sulphuric acid is always prepared from sulphur or from some sulphur compound which burns to sulphur dioxide on being heated in the air. In addition to platinum and other substances acting in the same way, there is another method of hastening the slow oxidation of sulphur dioxide and this method is also used in the manufacture of sulphuric acid. Since substances which have not yet been considered are used in making sulphuric acid by this other method, the details of the process will be described later.

Sulphuric acid prepared in any of these ways is a heavy, colorless liquid which flows slowly like oil and has a density of 1.853. The density is due to what is called *internal friction*; sulphuric acid, therefore, is a liquid with high internal friction. Sulphuric acid is soluble in water in all proportions, and so great an amount of heat is generated during the solution that strong sulphuric acid should always be diluted with great care. Water should never be poured into concentrated sulphuric acid, as explosions due to sudden generation

of steam are likely to occur with a spattering of the corrosive liquid. The acid should always be poured into water with constant stirring so that the heavier liquid cannot settle undissolved to the bottom of the vessel.

**169. Density of aqueous solutions.**—When sulphuric acid dissolves in water, a marked decrease in volume occurs. Take a closed glass tube about a meter long and 1 cm. in diameter, fill it one-third full of sulphuric acid and carefully pour water upon it. The water will float on the surface of the denser liquid. Now fill the tube to the top with water, wrap it in a cloth (because of the heat evolved), close the open end by holding a piece of rubber against it, and slowly invert the tube a few times so that the acid and water mix. Although a strong evolution of heat takes place and a corresponding expansion, it will be found that the actual volume of the solution is less than that of the separate liquids, and that, after cooling, the upper level of the solution is now several centimeters below the top of the tube.

Fig. 64 shows, as was shown with hydrochloric acid, the relation between density and percentage content. The curve has a rather unusual form and it is particularly remarkable that the greatest density is not at 100 per cent but at about 97 per cent.

DENSITY OF AQUEOUS SULPHURIC ACID AT 15°.

Per cent $\text{H}_2\text{SO}_4$ .	Density.	Per cent $\text{H}_2\text{SO}_4$ .	Density.
5.	1.033	55.	1.449
10.	1.068	60.	1.502
15.	1.105	65.	1.558
20.	1.142	70.	1.615
25.	1.182	75.	1.674
30.	1.222	80.	1.732
35.	1.264	85.	1.784
40.	1.307	90.	1.820
45.	1.351	95.	1.839
50.	1.399	100.	1.836

**170. Properties.**—Sulphuric acid is a very strong acid which acts corrosively and must therefore be handled carefully. It, too, has a strong attraction for water, though not so strong as that of sulphur trioxide.

Its attraction for water can be shown if a little acid is weighed in an open dish and allowed to stand for a short time. There is a marked increase in weight due to the absorption of water from the air. Sulphuric acid is used, therefore, in drying gases and other substances. A gas may be dried by bubbling it

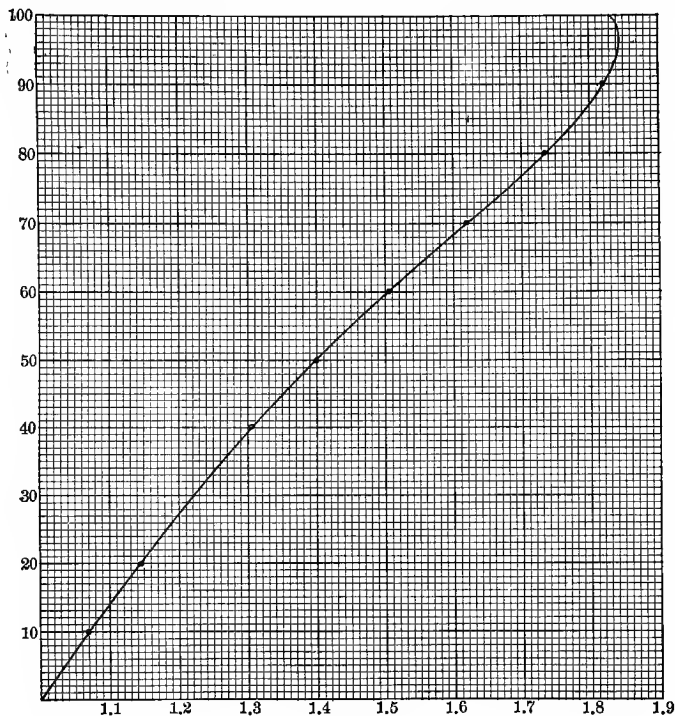


Fig. 64.

through sulphuric acid. Gas wash bottles, or briefly wash bottles, are used for such drying; a few of the common forms of such bottles are shown in Fig. 65. As compared with calcium chloride, sulphuric acid has the advantage of quicker and more powerful drying action, but on the other hand it is strongly corrosive, while calcium chloride is harmless. Instead of wash bottles, U tubes and towers, Fig. 66, filled with bits of pumice moistened with sulphuric acid, are often used for drying gases. They have the

advantage that they do not oppose any hydrostatic counter pressure to the gas flow.

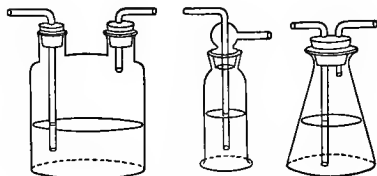


Fig. 65.

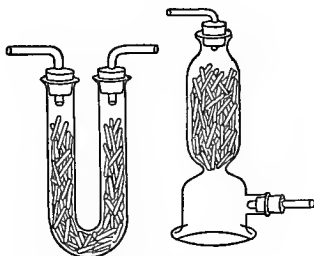


Fig. 66.

**171. Salt formation.** — The chief use of sulphuric acid depends on the fact that it is a strong acid and is not very volatile. It boils at  $360^{\circ}$ . If salts of other acids are warmed with sulphuric acid, a free acid is formed in most cases from the anion<sup>1</sup> of the salt, while the metal forms a sulphuric-acid salt, or sulphate. Sulphuric acid, then, is a general reagent for liberating acids from their salts. In order to understand this reaction fully, however, it is necessary to say a little more about sulphuric acid itself.

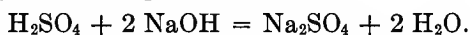
Whereas hydrochloric acid, or hydrogen chloride, contains, as its symbol,  $\text{HCl}$ , shows, only one combining weight of hydrogen, sulphuric acid contains two; and a study of the salts shows that both of these combining weights of hydrogen can be replaced by metals. There is, for example, the sodium salt,  $\text{Na}_2\text{SO}_4$ . Acids of this type, with two combining weights of hydrogen, are called *dibasic acids*. Sulphurous acid is also a dibasic acid.

It must first be proved that a dibasic acid can form a neutral salt as well as a monobasic acid can. Add a little litmus to some dilute sulphuric acid, to color it red, and add caustic soda solution until, at a definite point, the red color changes suddenly to blue. To carry out these observations quantitatively, weigh out a small amount of pure sulphuric acid

<sup>1</sup> The term *anion* indicates the acid constituent of the salt in contrast to the *cation* or metal of the salt. The cation is negatively charged with electricity and the anion is positively charged.

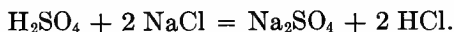
(about 1 g.) dilute with water, a step which can be taken without danger if a large amount of water is used, add the litmus, and neutralize the solution carefully with normal sodium hydroxide solution (p. 182) added from a burette. It will be found that for each gram of acid about 20 ccm. of sodium hydroxide are used; therefore to neutralize 1000 cc. of normal sodium hydroxide about 50 g. of sulphuric acid are needed.

The combining weight of sulphuric acid,  $\text{H}_2\text{SO}_4$ , is ( $\text{S}=32.07$ ,  $2\text{H}=2.02$ ,  $4\text{O}=64$ ) 98.09. It is evident, then, that only half of a combining weight of sulphuric acid is saturated by the weight of sodium contained in a liter of normal solution. The slight deviation from the theory is due to the fact that the commercial acid always contains a little water and it is very difficult to remove the last traces. For one combining weight of sulphuric acid (98.09 g.), therefore, two combining weights of sodium hydroxide are necessary and the equation reads



Since two combining weights of sodium hydroxide are used, two of water will be formed. It is not best to divide the equation by 2, for in this case the expression  $\frac{1}{2} \text{H}_2\text{SO}_4$  would be necessary, and we have already established the principle that it is undesirable to speak of half a combining weight or half an atomic weight.

**172. Action on salts of other acids.** — When sulphuric acid acts on salts, such a quantity of salt should be taken that the two combining weights of hydrogen in the sulphuric acid can be replaced by the metal. Thus, two combining weights of sodium chloride, or common salt, should be taken when it is to be decomposed by sulphuric acid. We have the equation



As is evident, this is a metathesis (p. 193). While the sodium replaces the hydrogen of the sulphuric acid, exactly as in the neutralization equation above, it is itself replaced by the hydrogen, and the resulting product is not water, as in the first case, but the compound  $\text{HCl}$ . This compound is, of course, the hydrochloric acid with which we are already familiar. To show this, place a

little common salt in a test tube and moisten it with sulphuric acid. The liquid foams and a colorless gas is generated; if the breath is blown across the mouth of the test tube, the characteristic cloud of aqueous hydrochloric acid is at once obtained. A drop of water on a stirring rod held over the tube dissolves the gas immediately, as is shown by the change in color of blue litmus when touched with the drop.

The above reaction is carried out on a large scale in the manufacture of hydrochloric acid; but in this case the decomposition usually takes place in bricked-up ovens so that all of the hydrochloric acid can be expelled by heat. The gas generated is led into large stone jars, which are filled with water and connected by wide tubes. The gas is dissolved in the water and forms ordinary aqueous hydrochloric acid. To collect the last traces of hydrochloric acid, which because of its corrosive action cannot be allowed to escape into the air, the gases are passed through fire-clay towers containing acid-proof tiles over which water trickles. The very large amount of wet surface exposed to the gas serves to effect its complete solution. The dilute acid made in this way is pumped back to a stone jar, to be saturated with the fresh acid. Here again is an application of the principle of *counter currents* which is so generally used in the arts (p. 57).

**173. Preparation of hydrogen chloride.**— We may use the above reaction to get a somewhat better knowledge of hydrogen chloride.

Since the gas is so quickly and freely dissolved by water it cannot, of course, be collected over water. It is difficult, too, to collect it simply by air displacement, as it is but slightly heavier than air. In such cases mercury may be used, because it is not attacked by pure hydrogen chloride. The discovery, early in the nineteenth century, of this use of mercury enabled the English chemist, Priestley, to discover a number of new gases. Among them was hydrogen chloride itself, which he prepared by the above method.

Place large lumps of common salt in a flask and insert a stopper which is provided with a dropping funnel and a gas outlet tube. Allow concentrated sulphuric acid to drop from the funnel



onto the salt until the air in the flask and the tubes is forced out by the hydrogen chloride. Collect the gas in inverted tubes filled with mercury and placed in a so-called "pneumatic trough" also containing mercury; the bottom of the trough is provided with a cylindrical depression for the tube that delivers the gas. Make sure that the collecting tubes are perfectly dry.

Hydrogen chloride is found to be colorless. By means of a pipette bent a little at the end, introduce a little water into one of the tubes; the mercury rises, showing that in spite of the reduced pressure the gas dissolves freely in water. If the gas is pure it will be completely dissolved; if impure, a gas bubble will be left.

Still keeping the tube with its mouth immersed in mercury, allow a small bit of magnesium to float up through the mercury into the aqueous solution. A violent evolution of hydrogen takes place because of the combination of the magnesium and chlorine. After a few minutes the generation of gas stops and it is found that about half of the tube is filled with hydrogen. Accurate experiments show that it is exactly half filled. This is a confirmation of the statement (p. 164) that hydrochloric acid is formed from equal volumes of hydrogen and chlorine, without any change in the total volume. If now, in the same way, the hydrogen in the acid could be kept back and the chlorine set free (no easy way of doing this is known) it would be found as before that half the cylinder would be filled with chlorine.

**174. The hydrogen content of acids.** — It is also important to know how much hydrogen can be generated from one cubic centimeter of a normal acid solution. For this purpose the apparatus shown in Fig. 37 (p. 119) may be used. Place a definite volume of normal hydrochloric acid (20 cc. for example) in the generating vessel. Introduce a few pieces of magnesium in the apparatus in such a way that they come in contact with the acid only when the tube is inverted. Now let the action take place and finally measure the volume of hydrogen evolved; it will be found that each cubic centimeter of acid generates about 12 centimeters of hydrogen. This number varies with the temperature and the barometric pressure, both of which, as is well known, have a marked influence on gas volumes.

A normal solution of sulphuric acid is made by adding a little more than 50 g. of the concentrated acid to a liter of water and titrating 20 cc. with normal sodium hydroxide and then diluting as required. Since, as has been stated, the sulphuric acid always contains water, somewhat more than half the combining weight of the acid was prescribed because in preparing an exactly normal solution it is easier to dilute than it is to remove an excess of water.

If, now, the same experiment (measurement of the amount of hydrogen evolved) is repeated using normal sulphuric acid instead of normal hydrochloric acid, it will be found that *equal volumes of the two acids evolve equal amounts of hydrogen*. This must necessarily be true, as the two solutions were prepared in such a way that each contained one combining weight, or 1.01 g., of hydrogen per liter. It is therefore immaterial whether the hydrogen was combined with chlorine or with  $\text{SO}_4$ , the anion of sulphuric acid; when it is replaced by magnesium (or any other metal) the same amount of hydrogen is liberated. Again, the amount of magnesium dissolved is naturally the same in each case. This can be shown by treating a large piece of magnesium with a measured amount of hydrochloric acid and afterwards with an equal volume of normal sulphuric as long as hydrogen is evolved. If the metal is weighed before and after each experiment (after careful drying) it will be found in each case to lose 1.2 grams for each 100 cc. of the normal acid.

**175. Sulphates.** — Salts of sulphuric acid are called *sulphates* and many of them are important substances in the arts and in medicine. Some of them also occur in nature as minerals. The anion  $\text{SO}_4$  is present in all of them, just as the element Cl is in all chlorides; it is known as the *sulphate ion*. Some sulphates are soluble in water, others are insoluble; in the latter class is the sulphate of barium, a metallic element somewhat like magnesium. Every time sulphuric acid or a sulphate comes in contact with a soluble barium salt, this insoluble salt, barium sulphate, is formed. The formula is  $\text{BaSO}_4$ , since barium, like magnesium, is bivalent.

Since this salt is insoluble in water or, more correctly stated,

very slightly soluble, it appears as a white, pulverulent precipitate whenever it is formed in solution. A barium salt, generally barium chloride,  $\text{BaCl}_2$ , is used, therefore, to detect the presence of sulphuric acid or sulphates in an unknown solution. The precipitate is formed even at great dilutions, so that barium chloride is a very sensitive reagent in testing for sulphuric acid and sulphates or, broadly speaking, for the sulphate ion. When this precipitate is formed it remains unchanged even after addition of hydrochloric acid. This is important, as there are a great many other difficultly soluble barium salts which form in neutral solution but are soluble in acids, particularly in hydrochloric acid. It can be shown in this way that most drinking water contains sulphates, for if such a water is first acidified with hydrochloric acid and then treated with barium chloride, a white turbidity forms which later settles to the bottom as a white precipitate. In like manner it can be shown that Glauber's salt is a *sulphate*, or salt of sulphuric acid.

**176. Glauber's salt.**—Sodium sulphate is called Glauber's salt after the German physician and chemist, Glauber, who described it in detail and first showed its valuable medicinal properties. He named it *sal mirabile*, or wonder salt. This afterwards became *sal mirabile Glauberi* and was finally shortened to Glauber's salt. The salt is obtained on the market in large crystals containing water of crystallization. As can be calculated from the symbol,  $\text{Na}_2\text{SO}_4 + 10 \text{H}_2\text{O}$ , more than half the weight of the solid is water. The crystals are usually coated at certain places with an opaque white powder, due to the fact that the crystals lose water easily. Whether this happens or not depends on the partial pressure of the water vapor in the air. If this is less than the vapor pressure of the water from the crystals, the latter will *weather*, *i.e.*, lose water; otherwise they stay unchanged. The vapor pressure of Glauber's salt is 0.63 that of water, so that air is dry enough to allow weathering when its humidity is less than 63 per cent. Weathering does not necessarily occur even then, for uninjured crystals will keep in even drier air. As soon as a trace of weathering product is present, however, the weathering goes further. The white

powder does not contain water of crystallization, but is anhydrous sodium sulphate. If Glauber's salt is heated in a flask, it appears to melt at  $32^{\circ}$ . It will be seen, however, that the liquid, even after long-continued heating, is not clear but that a solid is left in the bottom of the flask. At this temperature Glauber's salt breaks down into the anhydrous salt and a saturated solution, and since there is not enough water of crystallization to hold all the salt in solution, the excess separates out as a solid. If a little water is added, however, the solution becomes clear.

If now the flask is closed with a plug of cotton, or carefully covered with paper, taking pains not to leave any unmelted crystals in the neck of the flask, the liquid can be cooled to room temperature without any crystallization taking place (*cf.* p. 38). If the flask is then opened, crystallization occurs almost instantly and apparently spontaneously. With great care this can sometimes be avoided. The sudden crystallization depends on the fact that the dust of cities almost always contains Glauber's salt in small traces, and this falls into the solution when the flask is opened.

**177. Acid salts.**— If one combining weight of anhydrous sodium sulphate is heated with one combining weight of sulphuric acid (roughly 142 parts of the former and 98 parts of the latter), the mixture melts readily to a liquid, which, on cooling, hardens completely to a solid crystalline mass. This is a new sodium salt of sulphuric acid and is formed from the ordinary salt according to the following equation:



The salt  $\text{NaHSO}_4$  differs from Glauber's salt in having only one of the two atoms of hydrogen in sulphuric acid replaced by sodium, leaving the other still present. An aqueous solution of the salt, therefore, will react acid to litmus and will generate hydrogen from magnesium. This is a compound which is half neutral salt and half acid, and is called *sodium acid sulphate* or *sodium bisulphate*, while Glauber's salt is known as *neutral* or *normal sodium sulphate*. All dibasic acids are capable of

forming salts of this type. This is not true of the monobasic acids, as their formulas show that they contain only a single replaceable hydrogen atom instead of two.

Acid salts of bivalent metals are formed from two combining weights of acid and one of the metal, since otherwise no unreplaced hydrogen would be present. Acid magnesium sulphate, for example, has the formula  $MgH_2(SO_4)_2$ . Such salts are formed much less readily than those of the univalent metals.

The dibasic sulphurous acid (p. 200) can form acid salts in addition to normal salts in exactly the same way.

**178. Thiosulphates.**—In addition to sulphurous and sulphuric acids, sulphur forms a number of other acids with oxygen, all of which are dibasic and differ in respect to the relative amounts of sulphur and oxygen that they contain. Most of these substances are unimportant. The sodium salt of one of them, however, is made and used in large quantities. It is made by boiling sodium sulphite,  $Na_2SO_3$ , with sulphur. The sulphur dissolves and when the solution is evaporated a new salt having the composition  $Na_2S_2O_3 + 5 H_2O$  crystallizes out. Evidently one combining weight of sulphur has been taken up by the sodium sulphite. If one combining weight of O had been added to the sulphite, sodium sulphate would have been formed. The salt has, therefore, been named *sodium thiosulphate*, as it may be regarded as a sulphate in which one oxygen has been replaced by sulphur; *thion* is the Greek word for sulphur.

Sodium thiosulphate is much used in photography as a fixing salt, because it has the property of dissolving silver salts. Photography depends on the change which various silver salts undergo in the light, and when the negative has been developed the excess of silver salt must be removed so that it will not be subject to further change. For this purpose a solution of sodium thiosulphate is used to make the negative insensible to light or to "fix" it.

When heated, the salt melts in its water of crystallization without leaving an excess of the anhydrous salt, as happens with Glauber's salt. In the absence of dust the liquid can readily be supercooled and the experiments described on page 212 repeated.

If hydrochloric acid or sulphuric acid is added to a thiosulphate solution, sulphur soon separates and the liquid smells strongly of sulphur dioxide. The process which takes place here is the exact opposite to that which led to the formation of the salt. The free thiosulphuric acid is unstable and decomposes at once into sulphur and sulphur dioxide. If the solution is made alkaline by adding sodium hydroxide and is boiled for a short time the sulphur will dissolve again, with the formation of thiosulphate, which is stable in neutral or alkaline solutions.

**179. Hydrogen sulphide.**— From previously described experiments in which different metals like mercury and iron were caused to combine with sulphur, it is evident that sulphur acts towards the metals in much the same way as chlorine does. It was shown that the compounds of metals with chlorine are salts of these metals, because exactly the same compounds with identical properties are formed when hydrochloric acid acts on the hydroxides of the metals. In the latter case, water is formed at the same time because the chlorine of the acid is combined with hydrogen.

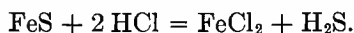
It is therefore to be expected that sulphur, too, will form with hydrogen an acid which with bases or metallic hydroxides gives salts and water. These salts should be exactly the same as those made by the direct combination of the metal and sulphur.

As a matter of fact, *hydrogen sulphide*, or sulphuretted hydrogen, has already been studied.<sup>1</sup> It was the gas smelling like rotten eggs that was generated in treating iron sulphide with hydrochloric acid (p. 105). In the same way that sulphuric acid drives hydrochloric acid out of sodium chloride, forming the sodium salt of sulphuric acid, called *sodium sulphate*, hydrochloric acid drives the hydrogen sulphide out of iron sulphide, leaving behind the chloride of iron, called *ferrous chloride*. The name *ferrous* indicates that iron can combine with more chlorine, a fact which will be studied more carefully later.

To write the corresponding equation, we must know that sulphur is bivalent and therefore unites with two combining

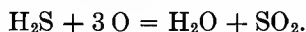
<sup>1</sup> The substance has been called *hydrosulphuric acid*, but this name is seldom used.

weights of hydrogen to form hydrogen sulphide. Iron is also bivalent. Ferrous sulphide is composed of one combining weight each of bivalent sulphur and bivalent iron and has the formula  $\text{FeS}$ . Similarly, ferrous chloride will contain two combining weights of univalent chlorine to one of iron and has the formula  $\text{FeCl}_2$ . The equation for the action of hydrochloric acid on iron sulphide is



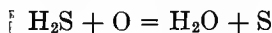
This reaction is used in the laboratory for preparing hydrogen sulphide, a substance of frequent use in testing for certain metals. Ferrous sulphide is made for the purpose by heating iron and sulphur together. Since the decomposition takes place rapidly enough in the cold, the same apparatus that was used for generating hydrogen may be used to make hydrogen sulphide.

**180. Properties.**—Hydrogen sulphide is a colorless gas slightly denser than air, and burns with a blue flame. In burning, the hydrogen forms water and the sulphur forms sulphur dioxide, according to the equation



If oxygen of the air is not furnished rapidly enough, or if the flame is chilled somewhat, only the hydrogen will burn and the unburned sulphur will settle out as a yellow deposit. This can be seen if a porcelain plate is held in the flame of burning hydrogen sulphide. The plate becomes covered with drops of water and at the same time with a film of yellow sulphur.

The same thing occurs if hydrogen sulphide is kept in contact with air, or oxygen, at ordinary temperatures. The equation



shows that the oxygen simply takes the sulphur away from its hydrogen. This is one of the cases in which oxygen acts chemically at low temperature; to be sure in this case also the reaction takes place very slowly.

The effect of the reaction is noticeable, however, when hydrogen sulphide is led into water and the resulting solution kept in contact with air. The gas is not nearly so soluble in water as hydrochloric acid is, and, in fact, at room temperature only about

3 volumes will dissolve in one volume of water. The solution is clear at first, but soon becomes cloudy owing to the separation of very finely divided sulphur, which, because of its fineness, looks almost white. If air has free access to the solution, soon all the hydrogen sulphide is oxidized.

Aqueous solutions of hydrogen sulphide are acid to litmus, but the acid properties are much weaker than in the case of hydrochloric acid, so that hydrogen sulphide is classed as a weak acid. Its salts are the metal sulphides. The sulphur compounds of the heavy metals are insoluble in water and have characteristic colors, black, red, yellow, etc., and are often used as indications of the presence of the corresponding metals in solutions of their soluble salts. The usefulness of hydrogen sulphide in chemical laboratories is based on this fact. The reactions will be studied later in connection with the different metals.

Hydrogen sulphide is also formed by the decay of animal substances, most of which contain sulphur. The albumin of eggs is particularly rich in sulphur, and hence, on putrefaction, hydrogen sulphide is formed comparatively easily and quickly from it. It should really be said, therefore, not that the gas smells like bad eggs but that bad eggs smell of hydrogen sulphide. Hydrogen sulphide is a poison to man and to the higher animals and shows its poisonous effect even when present in comparatively small quantities. Cases of suffocation from hydrogen sulphide occur frequently during the cleaning of cess-pools and similar places containing decaying organic matter. The best antidote is artificial respiration, exactly as in drowning. Accordingly, good ventilation is requisite in working with the gas, and would be desirable in any case because of the bad smell. In cases of poisoning the sense of smell is deadened so that one fails to note the odor at the time when it is most dangerous.

The salts of hydrogen sulphide are, as stated, simply the sulphur compounds of the metals. They are known as the *sulphides*, or, in order to distinguish between two compounds having different amounts of sulphur, as the higher and lower sulphides. The names persulphide and polysulphide are also used. In general the metallic sulphides are analogous to the oxides in com-



position, since sulphur, like oxygen, is bivalent with respect to the metals. There are a few exceptions, however.

The sulphur compounds of the heavy metals occur in Nature in large amounts and form important ores; in mineralogy they are known as pyrites, glances, and blendes. The pyrites are compounds looking almost like metals; with the glances, the metallic luster is less pronounced and in the blendes it is completely wanting. The various compounds will be named when the heavy metals are studied. The first step in recovering the metal from them is generally a *roasting*. The sulphur burns to sulphur dioxide, while the metal, as a rule, takes up oxygen and is changed to oxide. This latter is then reduced to the metal by heating with charcoal or with some other form of carbon. Formerly the sulphur dioxide was allowed to escape into the air, but at the present time it is generally converted into sulphuric acid, partly because of its value but chiefly to avoid injury to plant life caused by the presence of sulphur dioxide in the atmosphere.

The sulphides prepared in the laboratory from aqueous solutions usually look quite unlike the natural sulphides, as most of them contain water and are not crystalline. The sulphides of the heavy metals are insoluble and have characteristic colors, so that they can be used as a means of detecting the presence of the corresponding metal. The following colored sulphides are formed on adding hydrogen sulphide water to various salt solutions: *zinc*, white; *cadmium*, yellow; *antimony*, orange; *bismuth*, *lead*, and *copper*, brown to black.

#### § 24. THE ALKALINE EARTH METALS.

181. **Calcium.** — Calcium stands in the same relation to magnesium that potassium does to sodium. The combining weights give the first indication of this.

Na 23.00	Mg 24.32
K 39.10	Ca 40.09

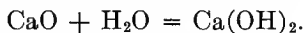
Calcium is a grayish-white, fairly tough metal, which for a long time was little known. Only comparatively recently has it

been prepared pure in large quantities by the electrolysis of its chloride. In the air, especially moist air, it soon becomes coated with a layer of oxide, and is completely oxidized eventually. It is much more readily oxidized than magnesium, exactly as potassium oxidizes more readily than sodium. It generates hydrogen freely when treated with water, violently when acids are used, and if ignited it burns with a brilliant flame. It has not yet found any commercial use.

**182. Lime.** — *Calcium oxide*,  $\text{CaO}$ , is made on a large scale by calcining natural limestone, which consists in exposing the mineral to a high temperature. The chemical reaction will be explained later. The product comes on the market under the name of *quicklime* or *caustic lime*. Pure calcium oxide is white, but because of impurities in raw materials, quicklime is usually gray or yellow in color.

If water is poured over quicklime, there seems to be no action at first. The mixture gradually heats up, however, particularly if the dish in which the experiment is carried on has been heated. Soon the water begins to combine with the lime with a hissing sound and more water is often needed to complete the reaction. The mass swells and bubbles considerably, and if not too much water has been used, a fine white powder is left, occupying a much greater space than the calcium oxide did and weighing about one-third more.

Since water is the only new substance present, the reaction must be considered as a union of calcium oxide with water, and a study of the weight relations shows that one combining weight of the former (56.09) has united with one (18.02) of the latter. It is, then, a relationship analogous to that of magnesium oxide and its hydroxide, except that in this case the reaction has generated a much greater amount of heat. The equation can be written:—



This process, which has been known for centuries, is known as the *slaking of lime*, and indicates the change of quicklime into *slaked lime* for use as mortar. When mortar is to be made,

enough water is used to form not only the hydroxide but to make a pasty mass.

*Calcium hydroxide* is a white, light powder which is slightly soluble in water. One liter of water will dissolve 2 g. of it. The solution is distinctly alkaline to litmus and will neutralize acids. It is made by shaking up a large amount of lime with water and allowing it to settle. The supernatant liquid is a saturated solution of calcium hydroxide in water and is called *lime water*. It is much used in medicine as well as in the laboratory.

Calcium hydroxide loses water when strongly heated and goes back to the oxide; the latter is, therefore, the anhydride of the hydroxide. On the other hand, the hydroxide may be considered a hydrate of the oxide, since any compound is called a hydrate which results when a substance takes up water, provided the water can be separated again by heating. All compounds containing water of crystallization may be considered as hydrates. The act of combining with water is known as *hydration*.

The strong affinity of calcium oxide for water makes it useful as a drying agent. If articles readily injured by water vapor are to be kept, they can be put in a closed space containing a few lumps of quicklime. This takes up the moisture and dries out the materials in question. The method is useful, as quicklime is inexpensive and very effective though its action is slow. It must be remembered in this connection that lime expands considerably on taking up water, and therefore enough space must be left for it.

Calcium oxide and calcium hydroxide dissolve readily in hydrochloric acid, with evolution of heat, and the resulting salt, calcium chloride, has already been mentioned. It crystallizes with water of crystallization but with amounts varying with the temperature (1 H<sub>2</sub>O to 6 H<sub>2</sub>O). The smaller quantity combines at the higher temperature. At white heat it loses all its water, and on cooling hardens to a crystalline mass. For drying purposes (p. 141) it is better not to use the melted salt but merely the dehydrated salt which is obtained in a spongy state by heating the crystals to a temperature slightly below the melting point.

In this form it takes up water vapor much more quickly than the melted salt because of the greater surface exposed.

**183. Gypsum.** — The sulphate of calcium,  $\text{CaSO}_4$ , is a salt that is only slightly soluble in water; in Nature it occurs abundantly in crystals with 2 molecules of  $\text{H}_2\text{O}$ , and is called *gypsum*. The crystals belong to the same family as the sulphur crystals with the higher melting point, *i.e.*, they are monoclinic and have only a single binary axis. They are characterized by the fact that they are not brittle but are remarkably pliable. The crystals often occur in a long series of parallel threads and are then known as fibrous gypsum, or *satın spar*. A more granular form that is translucent is known as *alabaster*; it is used for making small ornaments, as it is soft enough to be worked easily. If a sulphate is added to a moderately concentrated solution of a soluble calcium salt, a white precipitate is formed. Under the microscope this shows distinctly the monoclinic structure of gypsum prisms, often grown together in double crystals or twins, in which the oblique end surfaces join, making a reëntrant angle.

Gypsum loses its crystal water on moderate heating and changes to a chalky mass of anhydrous calcium sulphate known as *plaster of Paris*. If this is stirred with water, the water soon unites with it and the resulting crystals interlock in such a way that a coherent mass is formed. This property is utilized in making plaster casts. To illustrate, make a rim around a coin with a piece of paper, grease the coin slightly to facilitate the subsequent removal of the plaster, and pour upon it a freshly made paste of plaster of Paris. After from a few minutes to half an hour, dependent upon the extent to which the gypsum has been heated, the mass hardens. After the gypsum has become hard and dry, it can be easily removed and it will be found to bear a very exact imprint of the coin. Now by greasing the mold thus made and adding some more of the plaster of Paris, an exact imitation of the coin can be obtained. The hollow form is called the *matrix* or "mother form."

In complicated pieces the matrices are made from a number of pieces, so that they can be removed easily without danger

of breaking them or the cast. This is the reason for the slight lines or projections which are noticeable in large casts and which show the method of building up the complete figure.

In addition to its use in making casts, plaster of Paris is used in bandaging broken bones, in making imitation marble, and for other similar purposes. It cannot be used for objects exposed to moisture, as the plaster will dissolve in time and the figure fall to pieces.

The water of rivers and springs usually comes in contact with gypsum and often contains small amounts of it. The greater the amount of calcium and magnesium salts a water contains, the *harder* it is said to be. Hard water is unsuitable for boilers, as the salts are left on evaporation and form the injurious boiler scale. In many chemical processes, too, the presence of calcium sulphate is undesirable, as it sometimes causes objectionable chemical reactions to take place, *e.g.*, in washing or cooking.

Anhydrous calcium sulphate also occurs in nature as *anhydrite* (because it is the anhydride of gypsum) and is found under those conditions which would make gypsum lose water (high temperatures or the presence of dehydrating salts). Anhydrite does not combine with water directly as anhydrous gypsum does. It crystallizes in orthorhombic forms (p. 195), *i.e.*, its crystals have three binary axes of symmetry perpendicular to each other.

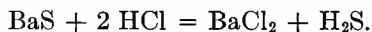
**184. Barium and strontium.** — Two other elements are closely allied to calcium in their properties, namely *strontium* and *barium*, with the combining weights  $Sr = 87.62$ ,  $Ba = 137.37$ . Although these metals are not infrequently found in Nature, they cannot be classed with the plentiful substances.

Metallic barium is much like calcium, though it oxidizes more easily and more quickly. It has not found any technical use. It occurs in Nature chiefly as the sulphate,  $BaSO_4$ , and the carbonate,  $BaCO_3$ . The former is called *heavy spar*<sup>1</sup> because of its unusually great density (4.5) and crystallizes in orthorhombic crystals, isomorphous with anhydrite or anhydrous calcium sulphate. Barium sulphate is practically insoluble in water and in acids, and always forms as a white precipitate when sulphuric

<sup>1</sup> Another name for the mineral  $BaSO_4$  is *barite*.

acid or a sulphate comes in contact with a soluble barium salt. We have already made use of the reaction for the detection of sulphuric acid. Barium sulphate is also used as a white pigment.

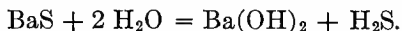
On account of its insolubility, it is not readily acted upon by most chemical agents. To "open it up" or convert it into a form more accessible to reagents, it may be heated with carbon, which reduces it to barium sulphide, the oxygen passing off as carbon monoxide. The barium sulphide, on being treated with acid, is readily converted into the corresponding barium salt and hydrogen sulphide is evolved, *e.g.*,



*Barium chloride* crystallizes in brilliant, fairly soluble crystals containing 2 H<sub>2</sub>O. As has been shown, its solution is used in testing for sulphates or, broadly speaking, for detecting the sulphate ion.

If strong nitric acid is added to a barium chloride solution, a precipitate is thrown down which might lead one to think that the nitric acid was contaminated with sulphuric acid. The precipitate is, however, barium nitrate Ba(NO<sub>3</sub>)<sub>2</sub>, which is not very soluble in water and much less soluble in nitric acid. The precipitate differs from barium sulphate in being much more coarsely crystalline and a moderate magnification shows isometric crystals. If the solution is decanted from the crystals and replaced by pure water, the barium nitrate goes into solution, which is, of course, not true of the sulphate.

If barium sulphide is heated in steam, hydrogen sulphide is driven off and *barium hydroxide* is formed.



Barium hydroxidé is fairly soluble in hot water and crystallizes on cooling with 8 H<sub>2</sub>O in the form of large needles. As it is much more soluble in cold water than calcium hydroxide, its solution, called *baryta water*, is used as a strongly alkaline reagent, like caustic soda or caustic potash. It has the advantage that it does not attack glass so easily as the caustic alkalies do.

Strontium lies between barium and calcium in its properties. Its sulphate is more soluble than barium sulphate but less so than calcium sulphate, and, conversely, its hydroxide is somewhat less soluble than barium hydroxide but dissolves more easily than lime. It occurs in Nature as the sulphate and, like the corresponding barium compound, crystallizes in the orthorhombic form. As mineral, it is called *celestite*.

Strontium compounds have the property of imparting a red color to a flame and for this reason are used in making fireworks. The hydroxide is used somewhat in separating sugar from the sugar-factory residues, but the chemical reactions would not be understood if explained here.

**185. Regularities in the atomic weights.**—The elements magnesium, calcium, barium, and strontium are called *alkaline earths* because, on the one hand, they resemble the alkalis in their strongly basic properties, and, on the other, play a large part in the formation of the earth's crust, especially the first two elements.

Their properties change progressively with their atomic weights. The solubility of the hydroxides increases with increasing atomic weight, while that of the sulphates decreases. The affinity of the free element for oxygen also increases with the atomic weight, for while magnesium can be kept in ordinary air, calcium requires dry air, and strontium and barium oxidize so easily that they can be kept only if air is excluded.

The numerical values of the combining weights run curiously parallel to those of the halogens and alkali metals, as the following table shows:

F	= 19.0	Cl	= 35.46	Br	= 79.92	I	= 126.92
Na	= 23.00	K	= 39.10	Rb	= 85.45	Cs	= 132.81
Mg	= 24.32	Ca	= 40.09	Sr	= 87.63	Ba	= 137.37

Two other metals (Rb = rubidium and Cs = cæsium) belong in the alkali series but, because of their rare occurrence, have not been mentioned before; they are introduced here to show the regularities in the series. To be sure the differences in the atomic weights are not exactly the same in corresponding columns nor

do they have any simple relationship, and still the regularities in the general arrangement are unmistakable, as in each of the groups (F, Na, Mg; Cl, K, Ca, etc.) the elements have atomic weights lying close together.

These regularities are special cases of a general law which deals with the combining weights of all the elements. The rule cannot be explained at this point, as its meaning is evident only when the properties of all the elements and their compounds can be considered.



## CHAPTER VIII.

### NITROGEN AND RELATED SUBSTANCES.

#### § 25. NITROGEN AND ITS OXYGEN COMPOUNDS.

**186. Nitrogen.** — This element has already been mentioned as one of the constituents of the atmosphere. It forms 79 per cent by volume of the air and largely determines its physical properties. It has, however, almost no influence on the chemical properties of air, as it is only under very special conditions that nitrogen will form compounds.

To make nitrogen from the air, the oxygen, water vapor, and carbon dioxide, which are always present, must be removed. The last two can be absorbed by sodium hydroxide, while the oxygen may be passed over some element with which it will unite. One whose oxide is not volatile is best suited for this purpose. Copper in the form of turnings or thin shavings has been found satisfactory, as when it is heated to 400° to 500° it takes up oxygen quickly and completely. In making the experiment, arrange the apparatus so that the air passes over sodium hydroxide, then over heated copper, and then collect the nitrogen. Atmospheric nitrogen contains about one per cent of another gas called *argon*, which cannot be made to act chemically. It is denser than nitrogen and therefore the density of nitrogen made from air is higher than that of pure nitrogen. Argon is, however, a perfectly inert gas and so does not affect the chemical properties of nitrogen. In order to free the latter from argon, chemical methods which cannot be discussed here are used.

Since, at the present time, the liquefaction of air is carried out on a technical scale, large amounts of atmospheric nitrogen are obtained either by fractional distillation of liquid air or by the fractional liquefaction of air, with a corresponding

separation of the constituents. These operations are exactly like those used in separating alcohol and water by distillation (*cf.* p. 77), except that with air the temperature is about 200° lower. Atmospheric nitrogen has lately become of considerable importance in the artificial production of nitrogen compounds.

Nitrogen is a little harder to liquefy than oxygen; it boils at  $-196^{\circ}$  under atmospheric pressure and is colorless in the liquid state. It is somewhat less soluble in water than oxygen is, so that water in contact with air contains relatively more oxygen than nitrogen.

**187. Nitrogen compounds.** — Although free nitrogen can be made to enter into combination with other elements only with difficulty, yet, after it once enters into chemical combination, a large number of compounds can be formed; these various nitrogen compounds can be changed easily into one another. Thus although free nitrogen has practically no money value, as it can be obtained from the air in any amount needed, *combined nitrogen* is comparatively expensive, costing roughly 12 cents a pound. The difference depends upon the fact that it takes a large amount of energy to change free nitrogen into the combined form, and the difference in price between 0 and 12 cents is based entirely on the energy content of combined nitrogen as compared with that of free nitrogen.

Combined nitrogen occurs in all plants and animals and is a constituent of the exceedingly important class of proteins, with the presence and transformation of which all life seems to be associated. Since plants are for the most part not able to take the necessary amount of nitrogen from the air, it must be furnished them in the combined form and in quantities large enough to nourish them. The increased fertility of fields and gardens depends largely on the amount of combined nitrogen added in the form of fertilizer. Plants need other elements, too, for their growth, particularly phosphorus and potassium. Nitrogen is the most costly of the three in proportion to the amount needed, so that the development of scientific farming depends largely on the cheapest possible production of nitrogen compounds.

Nitrogenous organic compounds may easily be recognized by the bad smell they give when burned. Burning hair, wool, meat, and milk show the presence of nitrogen in this way.

**188. Nitric acid.**—One of the most important nitrogen compounds is nitric acid, the sodium salt of which is found in large quantities on the rainless plateaus of Chili and is called Chili saltpeter. Almost all the nitric acid used in the present-day industries comes from this source. Chili saltpeter is also the most important nitrogenous fertilizer used in agriculture.

The scientific name of Chili saltpeter is *sodium nitrate*, as all nitric acid salts are called nitrates. The name comes from the Latin word for saltpeter, *nitrum*, and the Latin name of the element, *nitrogenium*, is derived from the same root. The method of making nitric acid is the same as that used in preparing hydrochloric acid; the nitrate is distilled with sulphuric acid forming sodium sulphate and nitric acid. Inasmuch as the latter acid is much more volatile than sulphuric acid, it can be separated by distillation.

Place some sodium nitrate in a tubulated retort, and connect the latter with a well-cooled flask. As nitric acid attacks all organic substances very strongly, all rubber and cork stoppers must be avoided and the acid allowed to come in contact with glass only. Distillation begins at a moderate heating, as nitric acid boils at 86°. The acid itself is colorless, but the retort and flask are soon filled with reddish-brown fumes. This is because pure nitric acid is not a very stable substance. It gives up its oxygen readily and goes over into a reddish-brown compound. For the same reason the distillate is more or less yellow. Strong light, especially, tends to decompose the acid and increase its yellowish-red color.

Nitric acid *fumes* in the air and heats up strongly when a little water is added. The reason is the same as with hydrochloric acid (p. 166); an aqueous nitric acid of 68 per cent has the highest boiling point and the lowest vapor pressure of all aqueous solutions of nitric acid. It is formed, therefore, by a union of the vapor from the strong acid with the moisture in the air and settles out in the form of mist. The solution boils

at 120°, and it is left to the last in distilling a stronger or weaker acid.

One drop of nitric acid in a large glass of water gives a solution which tastes acid and at once reddens litmus paper. It is, therefore, a strong acid and, in fact, is one of the strongest acids known. In addition to its acid properties, which it shares with hydrochloric, sulphuric, and other strong acids, it has other properties depending on the ease with which it gives up its oxygen; *i.e.* it acts as a strong oxidizing agent. If, for example, a glowing coal is dipped in the concentrated acid, the glow increases almost as if the coal had been dipped in pure oxygen. At the same time the nitric acid reduction products are given off in the shape of suffocating, bad smelling, red vapors. (Caution!)

Because of this oxidizing action, nitric acid has been found to be an effective reagent in dissolving certain metals that resist the action of other acids. Copper, mercury, lead, and silver cannot expel hydrogen from the acids; if pieces of these metals are treated with hydrochloric acid or sulphuric acid, they remain unchanged. If, on the contrary, the same metals are treated with not too concentrated nitric acid, an evolution of gas at once takes place and the metals dissolve. The gas in this case is not hydrogen but is one of the lower oxides of nitrogen. It cannot be burned, is colored brown, and its strong and unpleasant odor shows it to be a new substance.

The reaction consists, to be sure, of the replacement of the hydrogen in the nitric acid by a metal; hydrogen is not evolved, however, but is oxidized to water by the oxygen of the nitric acid. It is much easier to displace hydrogen in this way, and the reaction succeeds with metals that cannot drive out hydrogen as a gas from acids.<sup>1</sup>

Nitric acid, therefore, is used as a *solvent* and as an *etching medium* for metals. For instance, a copper engraving plate is made by covering the plate with a substance not attacked by nitric acid, the necessary drawing is made with a needle, and then

<sup>1</sup> Many chemists prefer to explain the reaction on the assumption that the nitric acid first oxidizes the copper to cupric oxide, CuO, which then dissolves to form cupric nitrate.

the surface is etched with nitric acid. Wherever the needle has exposed the copper, the metal is attacked by the acid so that lines are made. If now the whole surface is cleaned and polished and a printing color rubbed into the depressions, a copy of the drawing may be made by pressing the plate against soft "copperplate paper." Such a process is technically known as *etching*.

Nitric acid acts on organic matter partly as an oxidizing agent but it also forms characteristic organic compounds. The yellow spots formed on the fingers when the acid comes in contact with the skin are due to such *nitro compounds*, most of which are yellow.

**189. Nitrates.** — Nitric acid has the composition  $\text{HNO}_3$  and is therefore monobasic. The group  $\text{NO}_3$  is called the *nitrate ion*. A nitrate, then, has the formula  $\text{MNO}_3$ , where M represents any univalent metal. The nitrate of a bivalent metal must contain the nitrate group twice, and it has, therefore, the formula  $\text{M}(\text{NO}_3)_2$ . Sodium nitrate is  $\text{NaNO}_3$  and calcium nitrate is  $\text{Ca}(\text{NO}_3)_2$ .

The most important nitrate is sodium nitrate, or Chili saltpeter, and has already been mentioned. This salt crystallizes in large rhombohedrons which have a ternary axis of symmetry. If such a rhombohedron is held with the short axis vertical, the figure comes into a coincident position after every revolution through  $120^\circ$ . All secondary surfaces which occur in the crystals, also show this threefold symmetry. The corresponding crystal system which is characterized by a ternary axis of symmetry is called the orthorhombic system. Fig. 67 shows a rhombohedron viewed in the direction of its symmetry axis. This picture is apparently exactly like that of the cube (p. 188, Fig. 59), as in both cases we have a ternary axis. In the rhombohedron, however, only one such axis is present, whereas in the cube four axes of equal value are found. The rhombohedron could be made from the cube by extending or compressing it along one of its axes.

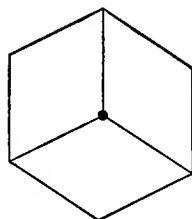


Fig. 67.

Of the other nitrates, the potassium salt should be mentioned, for it has been known from ancient times as *saltpeter*. It is formed by the oxidation of nitrogenous animal excreta in the air and a

subsequent union with the potassium salts occurring in the ashes of wood and other plants. The conditions for its formation were fulfilled, therefore, at the very beginning of human culture, where ashes and animal refuse were heaped up near settlements. As saltpeter crystallizes easily, it was obtained fairly pure even in the earliest times. Its chief importance is due to its use in making gunpowder. For this purpose combustible substances (sulphur and carbon) are mixed with an oxygen-rich substance (saltpeter) so that a strong chemical reaction may take place in a confined space. If the mixture is ignited a large volume of gas is formed, and this, at the high temperature, causes a high pressure by which the bullet, as the least resisting body, is driven from the gun barrel. This process deals with the transformation of chemical energy into mechanical energy (energy of motion), and the fundamental difference between a gun and a steam engine is that in the former the oxygen for the combustion is not taken from the air but is contained in the powder itself. The mechanical part of the process can be carried out very easily, as the only apparatus required is a cylindrical tube of sufficiently great resistance. The operation is expensive, however, as the oxygen in saltpeter is not as cheap as that of the air.

Explosion motors, in which a mixture of a combustible gas or vapor is burned with air in the cylinder, form a transition stage between the steam engine and the gun, as here too an explosive mixture is ignited in a closed space, though in this second case atmospheric oxygen is used. These engines operate well and cheaply and are largely used for motor vehicles, airships, and motor boats.

**190. Separation by crystallization.** — When saltpeter is formed as described above, it is usually mixed with common salt which originated in human food, and passed unchanged into the waste products of the body. The method of separating mixed salts by taking advantage of their different solubilities was devised for these two salts in the very earliest times.

The solubility curves of the two salts (Fig. 28, p. 84) show that at low temperatures common salt is much more soluble than saltpeter, whereas at higher temperatures the reverse is true.

This is because the solubility of common salt scarcely changes with the temperature, while that of saltpeter increases rapidly.

After leaching out the earth that is rich in saltpeter (using the principle of countercurrents) enough water can be evaporated so that the less soluble common salt is obtained from the hot solution as a solid. The process may be continued, with the occasional removal of the crystallized salt, until finally the solution is nearly saturated with saltpeter. If the solution, freed from much of the common salt, is now allowed to cool, practically nothing but saltpeter will separate, as the solubility of the common salt scarcely diminishes on cooling. The fairly pure saltpeter, which forms on cooling, is separated from the mother liquor, and the latter is evaporated further by heating. It will still contain relatively more common salt than saltpeter, but the two constituents can be separated by a continuation of the above process.

The partly purified saltpeter is redissolved in hot water and again allowed to crystallize on cooling; the common salt residues are left in the mother liquor. The latter is added to the crude liquor and evaporated with it; in such manner the purification can be carried as far as is desired in any given case.

Even when the nitrate crystals do not actually contain sodium chloride, as the latter crystallizes independently, they are nevertheless wet with mother liquor which does contain sodium chloride. To remove this without dissolving the salt again, water as cold as possible, or else pure nitric acid, is used. In this way sodium chloride is washed out and little or no saltpeter is dissolved. Since, however, a part of the mother liquor is mechanically held in the crystal, and cannot be reached by the wash liquor, a recrystallization is necessary for complete purification. Inclosed substances are most easily avoided if the crystals are not allowed to grow large. Small crystals are formed by stirring during evaporation. On the other hand, the moist surface would be too great if too fine a powder is formed. In this technical process, as in all others, it is necessary to choose between two extremes that middle way which leads most quickly and satisfactorily to the end in view. In the

discovery and perfection of such processes lies the progress of technical chemistry. To find these best ways, the fundamental law must be observed, that *those processes always require the least expenditure of work in which the least possible differences (of temperature, of concentration, or of pressure, etc.) take place.* The principle of *countercurrents* is an example of this law. Since, on the other hand, reactions usually go more slowly the smaller these differences are, an average should be found and no greater differences used than are needed to keep the reaction going.

The details of such a process can best be learned by carrying out the separation of a mixture of this kind (for instance, equal parts of common salt and saltpeter).

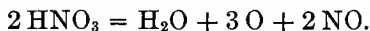
**191. Identification of nitrates.** — The salts of nitric acid, or the nitrates, can be made by all the usual ways of forming salts. The most obvious way is by the action of the free acid on the oxides, or hydroxides, of the metals. All normal nitrates are soluble in water, whereas most other acids form certain characteristic insoluble salts. For this reason there is no precipitation reaction to indicate the presence of nitrates in the way that the formation of barium sulphate shows sulphates. The nitrates can easily be recognized, however, by their high oxygen content, which causes a sudden brilliant flash when a nitrate is thrown on glowing carbon. This property does not belong to nitrates alone but is shown by other substances rich in oxygen, as, for instance, potassium chlorate. A surer indication of a nitrate is the evolution of brown fumes when treated with sulphuric acid and copper filings. The sulphuric acid decomposes the nitrate, forming nitric acid, which in turn acts on copper as described above.

A combustion by means of the combined oxygen in the nitrate may be shown in a striking manner by the following experiment. Place a little saltpeter in a small round-bottomed flask and heat over a powerful burner until the salt begins to decompose, as is indicated by the generation of gas bubbles. Now drop in a piece of sulphur not larger than a pea; it takes fire immediately and burns with an intensely white flame. Very soon red vapors are seen in the flask, due to the formation of sulphuric acid with

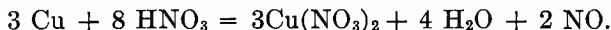


a corresponding partial reduction of the nitric acid, whereby the red vapors are formed.

**192. Nitric oxide and nitrogen peroxide.**—The brown vapors formed when nitric acid acts as an oxidizing agent are composed of different oxides of nitrogen, of which we shall study a few important ones. When copper turnings are treated with nitric acid (sp. gr. 1.3) reddish-brown fumes are freely evolved; these fumes become colorless when collected over water, and cannot be distinguished from air. The gas is nitric oxide and its formation from nitric acid is represented by the equation



It must be remembered, however, that the oxygen is not evolved but enters into chemical combination. In the case of copper, for example, it unites with the hydrogen of the nitric acid, so that the reaction for this particular case may be written



To make this equation clear, it should be noted that copper, Cu, is bivalent and thus combines with two combining weights of nitrate ions.

Nitric oxide, NO, is a gas which shows neither acid nor basic properties; it is only slightly soluble in water, and resembles nitrogen in its physical properties. Its behavior towards oxygen is remarkable. If oxygen is introduced in single bubbles into the gas which is confined over water, a reddish-brown cloud first forms, but disappears on shaking, with a simultaneous reduction in the volume of the gas, even though more oxygen is added. By the cautious addition of still more oxygen, almost the entire volume of gas can be made to disappear. The only gas remaining is due to the small amount of gaseous impurities usually present in oxygen and in nitric oxide. If the same experiment is made without water, as can easily be done by opening a cylinder of nitric oxide in the air, a similar reddish-brown cloud forms at once but does not disappear.

The union of nitric oxide and oxygen results in the formation of a new gas with reddish-brown color which is easily soluble

in water. This gas is called *nitrogen peroxide* and has the composition  $\text{NO}_2$ , containing twice as much oxygen as nitric oxide. Nitric acid is found in the water solution, and if enough oxygen is added, all the nitric oxide can be changed to nitric acid. The chemical reaction shown on page 233 has taken place in the reverse direction; the substances written on the right-hand side of the equation have disappeared and the substance on the left has been formed. There is one important difference, however, namely, that the oxygen is really added in the free state in this case, whereas in the former case it was considered to be combined.

These reactions are especially interesting, as a present-day method of changing free nitrogen to the combined form is based upon them. If an electric discharge is passed through air, so much heat is produced in its track that oxygen and nitrogen can be made to combine. For this reaction, as was stated on page 226, a considerable expenditure of energy is needed, and this energy is furnished by the discharge. The nitric oxide first formed picks up more oxygen and goes over into the peroxide, and if the gas mixture, which still contains a large amount of free oxygen (since the compound has used but a few per cent), is treated with water in large condensing towers, it changes to nitric acid. Inasmuch as the supply of Chili saltpeter is limited, and will not supply the world's demands indefinitely, this independent production of nitric acid is of importance. The manufacture of nitric acid in this way is costly, and the electrical energy needed to make the nitrogen enter into combination is also growing more expensive. It would, therefore, be more economical if the great stores of combined nitrogen which still exist in fossil coal and other organic deposits as well as in the refuse from cities, could be utilized regularly, as is done to-day to only a limited extent.

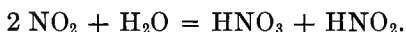
Nitrogen peroxide is a gas the color of which changes markedly with the temperature. If it is sealed in a glass tube, it appears light colored at ordinary temperatures, but becomes much darker on moderate heating. By preparing two similar tubes, the difference can be well shown by heating one tube and leaving the other cold. Nitrogen peroxide is most easily prepared for this

purpose by heating lead nitrate. A mixture of nitrogen peroxide and oxygen is formed according to the equation



As nitrogen peroxide can be liquefied by moderate cooling, this may be used as a means of separating it from oxygen, though for the experiment described above, this is not necessary.

**193. Nitrous acid.** — When water acts on nitrogen peroxide, nitric acid is eventually formed by the continued action of atmospheric oxygen. The first reaction with water, however, is somewhat different, and is represented by the equation



There is formed, in addition to the nitric acid, another acid containing one less oxygen atom. It is called *nitrous acid* and its salts are *nitrites*. The acid is not known in the free state, as it partially decomposes, even in aqueous solutions, with an evolution of nitric oxide (p. 233). It does form salts, however, some of which are of technical importance.

Such salts are easily obtained by treating sodium nitrate with a reducing agent. By the loss of one atom of oxygen, this salt changes into the corresponding nitrite. The reducing agent must, of course, be of such a nature that the removal of oxygen does not go too far; metallic lead has been found most suitable for the purpose. Formerly potassium nitrite, a yellowish, readily fusible substance, usually found on the market in stick form, was made in largest amounts, but to-day the cheaper sodium nitrite has largely replaced it. Both salts are readily soluble in water, and differ from the nitrates in producing brown fumes at once when treated with dilute sulphuric acid, whereas with the nitrates the addition of a reducing agent is necessary.

The technical uses of the nitrites lie wholly in the field of organic chemistry, where they are needed in the formation of countless artificial dyestuffs from coal-tar products.

**194. Nitrogen oxides in the manufacture of sulphuric acid.** — The mutual transformations of the oxides of nitrogen play an important part in the manufacture of sulphuric acid from sulphur

dioxide. It has already been stated (p. 203) that, in addition to platinum and other substances which similarly hasten the formation of the trioxide from the dioxide, still another sort of oxidation exists. This is the oxidation by the *oxides of nitrogen*.

Sulphuric acid was first made by exposing aqueous solutions of sulphurous acid to the action of atmospheric oxygen. This process was so slow that attempts were made to hasten it by getting the necessary oxygen from saltpeter or by burning a mixture of sulphur and saltpeter in a closed space containing water. It was found that very small amounts of saltpeter sufficed to produce large amounts of sulphuric acid. The oxygen of the nitrate was far too small in amount to have accomplished the complete oxidation, and so the question arose as to what actually did happen in the process.

The answer is given by the following experiment. Burn some sulphur in a large, moist flask which has been heated a little; then dip a glass rod in concentrated nitric acid and introduce the rod into the flask. Brownish fumes are formed at once, showing that the nitric acid has been reduced and a part of the sulphur dioxide oxidized. If the flask is allowed to stand for some time, the brown vapors will spread through the entire flask, and if finally the liquid is tested with barium chloride solution, the formation of a dense white precipitate shows the formation of considerable sulphuric acid. In this case, too, the small amount of nitric acid has formed an incomparably larger amount of sulphuric acid in the following way.

The sulphurous acid (or mixture of sulphur dioxide and water) first reduces the nitric acid to nitric oxide according to the equation given on page 233. The nitric oxide at once takes up oxygen from the air in the flask and changes to nitrogen peroxide. This oxidizes a fresh portion of sulphurous acid and is thereby reduced to nitric oxide. This again takes up free oxygen and is oxidized anew. In this way, by alternate oxidations and reductions, the oxygen of the air is made to unite with the sulphurous acid. The latter is changed thereby to sulphuric acid, and since the nitric oxides are not used up but can be brought back to their original condition repeatedly, a limited amount of nitric oxide

can convert any desired quantity of sulphurous acid to sulphuric acid.<sup>1</sup>

It is natural to ask why this roundabout way, through the oxides of nitrogen, is necessary in making sulphuric acid. The answer is that the method is indeed a long one with respect to the number of chemical reactions that take place but is not long with respect to the time required. The process takes place much more quickly than a direct oxidation of sulphurous acid by free, atmospheric oxygen, and for this reason is generally used. If a further question is asked as to why this reaction with the oxides of nitrogen does go more quickly it must be said that, up to the present time, science has not answered the question. Science now knows the facts but not the reasons. These, too, will be learned later.

Technically, this reaction is carried out on a very large scale, as by far the largest part of commercial sulphuric acid is made in this way. Sulphur dioxide was formerly made by burning sulphur. Free sulphur is seldom used now, as its place has been taken by sulphides, chiefly iron pyrites. The sulphur dioxide made by roasting other sulphide ores is also used at times. The hot gases containing an excess of oxygen are first led into a tower (the Glover tower) through which dilute sulphuric acid containing oxides of nitrogen is trickling. The gas is cooled off in this way and saturated with water vapor, while at the same time the sulphuric acid in the tower is concentrated and freed from the oxides of nitrogen. The gases then pass into chambers made of lead plates and just enough of the oxides of nitrogen (in the form of nitric acid) is added to make the oxidation quick enough. Water is also introduced into the lead chambers as a fine spray. The oxidation takes place completely only when a sufficiently large quantity of water is present, and an acid of about 60 per cent, the so-called "chamber acid," is obtained. The escaping gases, which still contain valuable oxides of nitrogen, are led through a second

<sup>1</sup> This simple explanation does not correspond exactly to the reactions that take place in the technical manufacture of sulphuric acid, but the principles involved are the same.

tower, the Gay-Lussac tower, in which they bubble through concentrated sulphuric acid. This takes out the nitric oxides very completely, so that practically nothing but nitrogen escapes into the air. The acid from the Gay-Lussac tower, which is now saturated with oxides of nitrogen and is called *nitrose*, goes back together with the chamber acid to the first tower.

All possible care is taken in the process to return all the oxides of nitrogen to their original condition in the cycle, but a certain part is always lost, partly by being reduced to nitrogen which cannot enter into the reaction, and partly through mechanical losses.

The chamber acid is frequently used directly, particularly if the sulphuric acid plant is only working to furnish acid which may be used in the crude form for other operations. If it is to be transported, it is concentrated to reduce weight as much as possible. For this purpose lead pans are first used, as they are not materially attacked until the solution contains 78 per cent of acid. Further concentration is carried out in platinum retorts. Nearly pure water distills until the acid is almost anhydrous. It cannot be completely freed from water in this way but always retains 1.5 per cent. A solution of this concentration distills unchanged and therefore forms the extreme limit of concentration by evaporation. The commercial acid usually contains a little more water.

## § 26. OXYGEN COMPOUNDS OF THE HALOGENS.

**195. Hypochlorites.** — Besides the salts which the halogens form by direct union with the metals, there is another series of salts which are related to oxygen acids like nitric acid. Some of these salts are of great importance, so that the group will be considered here in connection with the oxides of nitrogen.

If chlorine is led into solutions of caustic potash, or if it is allowed to act on some other base, a compound is formed and the chlorine is absorbed with the loss of its odor. If the solution is now allowed to crystallize, potassium chloride separates out and a salt that does not crystallize readily is left in the mother liquor. It has the composition  $\text{KOC}\text{l}$  and the reaction is



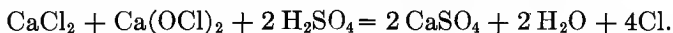
There is formed, therefore, in addition to potassium chloride the salt of a new monobasic acid; the latter has the symbol HOCl and is called *hypochlorous acid*. The salts are *hypochlorites* and OCl is the univalent hypochlorous ion.

Exactly the same reaction takes place when another base is used instead of potassium, for evidently the symbol K can be replaced in the salt by that of any other metal without changing the nature of the process. It is only necessary to change the proportions to correspond to the combining weights of the metals of a higher valence.

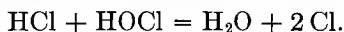
Thus the reaction is carried out with lime on a very large scale according to the reaction



The mixture of calcium chloride and calcium hypochlorite formed by this reaction is called *chloride of lime*<sup>1</sup> and is made by passing chlorine over slaked lime, which is spread out on a floor to permit the greatest possible absorption. A dry, white powder is obtained in this way, which, because of the calcium chloride present, soon becomes moist in the air and smells strongly of chlorine. The latter fact is due to a decomposition that the substance undergoes when acted upon by an acid and by which as much chlorine is set free as was originally used in making the chloride of lime. The reaction with sulphuric acid is



The process may be considered to proceed in such a way that hydrochloric and hypochlorous acids are formed first, which in turn react together to form water and set free chlorine.



Even very weak acids can cause this reaction to take place. It is true that they liberate only a very small amount of hydrochloric acid, but it is enough to start the second reaction, and when

<sup>1</sup> The exact chemical composition of *chloride of lime* has been the subject of much controversy and the question cannot be regarded as settled. Many chemists assume that the symbol  $\text{Ca} \begin{array}{l} \nearrow \text{Cl} \\ \searrow \text{OCl} \end{array} \cdot \text{H}_2\text{O}$  best represents the freshly prepared product.

the first amount of hydrochloric acid is used up the weak acid will form a second quantity. This is the reason that chloride of lime smells of chlorine when exposed to air which contains an acid (p. 254).

The hypochlorites, chiefly chloride of lime, but to some extent solutions made by conducting chlorine into caustic soda or potash, are used for all processes needing free chlorine, principally, of course, for bleaching, but also for disinfecting, oxidizing, etc.

In bleaching, for instance, the fabric or raw material is treated with a dilute solution of chloride of lime and then run through dilute sulphuric acid to cause the liberation of chlorine. As free chlorine sticks very tenaciously, extra care must be taken to remove it. This may be done by washing, or by treating with sodium sulphite or thiosulphate, both of which use up the excess chlorine and are oxidized. The last mentioned salt is often called *antichlor* because of its use in this reaction.

Evidently, nothing is gained in a chemical sense by first combining chlorine with lime and then freeing it by treatment with acid, for only as much chlorine can be liberated in the latter reaction as was required in the former. The advantage is wholly on the technical side, for chloride of lime can be transported in wooden casks handled without the troublesome smell of chlorine, and the chlorine can be freed at exactly the right time and in the amount needed. All these things are impossible with free chlorine, so it is combined with lime to make it more easily handled. The advantage of combining it as hypochlorite is that it may be liberated by the weakest acids.

The hypochlorites are scarcely known at all in the pure state, as they are all very soluble and crystallize badly; they are also unstable and lose their oxygen on standing. Chloride of lime also loses its chlorine and constantly grows less effective.

**196. Chlorates.** — Besides the hypochlorites there are other oxygen compounds of the halogens formed under slightly different conditions. If concentrated caustic potash is used for the experiment (p. 238) and chlorine is introduced into the hot liquid until no more gas is absorbed a salt crystallizes on cooling which can be prepared very pure by filtering, drying, and recrystallizing



from hot water. It is so much more soluble in hot water than in cold that if only enough water is used to dissolve it at boiling temperature the greater part of the salt separates on cooling and the mother liquor contains all the impurities with only a very small proportion of the salt.

The salt is well known to us already, for it is the potassium chlorate which was used in making oxygen. The chemical reaction for its formation is represented by the following equation:



Exactly the same number of combining weights of potassium hydroxide and chlorine react here as in the formation of hypochlorites, but in that case only one atom of oxygen combined with the chlorine, while in this reaction three atoms are used. The corresponding acid has the composition  $\text{HClO}_3$  and is called *chloric acid*. It is very similar to nitric acid in its formula and in its other properties. The conditions under which chlorates are formed instead of hypochlorites are given above. These are greater concentration, higher temperature, and, above all, an excess of chlorine. For this reason the reaction takes place at the end of the process after the hypochlorites have been formed.

Potassium chlorate loses its oxygen much less easily than the hypochlorite, for we have seen that the dry salt must be heated above its melting point. No decomposition occurs when its aqueous solution is boiled. The stability of the oxygen compounds of chlorine increases, therefore, with increasing oxygen content. Another example of this fact will be studied later.

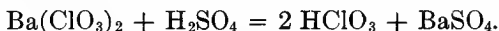
Potassium chlorate is technically prepared on a large scale and the chlorine needed is generated by electrolysis. The chlorine is not collected first but is made to act on potassium hydroxide present in the solution in which the chlorine is being formed.

The value of potassium chlorate depends on its oxygen content. It is used as an oxidizing agent in dyehouses and in other industries. Concentrated hydrochloric acid liberates chlorine and is itself colored yellow. Dilute acid does not affect the salt.

At present potassium chlorate is being more and more displaced by the more soluble sodium salt which is also easier to prepare. The salt crystallizes free from water and in isometric

crystals. Other chlorates will not be considered. All have the property of going over to chlorides on heating, with a loss of oxygen, and all are soluble in water.

A solution of free chloric acid can be prepared by treating a solution of barium chlorate with just enough sulphuric acid to change the barium completely to barium sulphate. A normal sulphuric acid solution (p. 210) containing 98.09 g. of acid in two liters is most convenient for this purpose. The molecular weight of barium chlorate,  $\text{Ba}(\text{ClO}_3)_2$  is 304.29, so that 304.29 g. of it will be decomposed by 2 liters of normal sulphuric acid, according to the equation



A suitable amount of the salt (30.429 g. for instance) is taken and treated with the necessary amount (in this case 200 cc.) of normal sulphuric acid solution; the salt is ground to a fine powder and the acid poured over it. The decomposition is hastened by shaking, and after a time a solution of chloric acid is obtained containing barium sulphate as a white insoluble powder. The liquid, on being decanted from the barium sulphate, is clear, but soon begins to smell of chlorine, as the free acid is very unstable and decomposes spontaneously into chlorine, oxygen, and perchloric acid (p. 243). Chloric acid is a strong acid, much like nitric acid.

This method of preparing a free acid by precipitating its barium salt with sulphuric acid is applied in those cases in which the free acid cannot be separated either by distillation or crystallization from the salts formed at the same time. Chloric acid would decompose at once on boiling and can be prepared only at a low temperature. The method of preparation is applicable to all nonvolatile acids which are soluble in water. It can be made more general by using some other base which will form an insoluble salt with a strong acid. For instance the corresponding acids may be prepared from the silver salts by treatment with hydrochloric acid, as silver chloride is insoluble.

**197. Perchlorates.** — If potassium chlorate is heated cautiously until oxygen just begins to be evolved, and is kept at this temperature for some time (30 minutes to 1 hour), a solid substance soon begins to separate from the molten salt and the

whole mass becomes almost solid. If the melt is now cooled, powdered, and extracted with cold water, a salt is left which is only slightly soluble in cold water and which may be purified easily by crystallization from hot water. It has the composition  $\text{KClO}_4$  and is called *potassium perchlorate*. It is formed from the chlorate according to the equation  $4 \text{KClO}_3 = 3 \text{KClO}_4 + \text{KCl}$ , but this reaction never takes place without a partial decomposition of the chlorate into the chloride and oxygen. By distilling the salt with sulphuric acid, the corresponding perchloric acid is obtained; it has the symbol  $\text{HClO}_4$ . This acid is much less easily decomposed than chloric acid and, dissolved in a little water, resembles concentrated sulphuric acid in appearance.

Because of the slight solubility of the potassium salt (1:60 at room temperature) the free acid, or its readily soluble sodium salt, has been used for precipitating and identifying potassium compounds, but its solubility is still too great to give sufficient sensitiveness. These compounds have practically no technical use.<sup>1</sup> It should be mentioned that sodium perchlorate occurs in Chili saltpeter, in which it is an undesirable constituent, as it acts injuriously on growing plants.

**198. Oxygen compounds of bromine.** — Bromine forms oxygen compounds similar to the corresponding chlorine compounds, but they are much less useful. Bases treated with bromine in the cold form bromides and hypobromites; the latter correspond in composition to the hypochlorites; they are colored yellow and like the hypochlorites crystallize badly. A yellow solution of bromine in sodium hydroxide is often used as an oxidizing agent. Dissolve 8 g. of sodium hydroxide in 100 cc. of water, add 2 cc. of bromine to the cold solution, and dissolve by shaking. The solution of the bromine takes place according to the equation  $2 \text{NaOH} + 2 \text{Br} = \text{NaBr} + \text{NaBrO} + \text{H}_2\text{O}$ , and the solution contains hypobromite as well as bromide. It behaves exactly like the corresponding chlorine compound.

Bromine also forms bromic acid and the corresponding bromates which are similar to the chlorates. If slightly more than

<sup>1</sup> Very recently an attempt has been made to use them in the manufacture of explosives.

the equivalent amount of bromine is added to a concentrated potassium hydroxide solution, it dissolves with a strong evolution of heat, and on cooling the slightly soluble potassium bromate,  $\text{KBrO}_3$ , soon begins to separate from the solution. The experiment is easier to perform than the similar one with chlorine, as liquid bromine can be added much more quickly than gaseous chlorine. *Perbromates* are not known.

**199. Oxygen compounds of Iodine.** — When iodine dissolves in dilute alkali, there is formed, in addition to the iodide, a hypo-iodite which soon changes to the iodate. Free *iodic acid* can also be made by the oxidation of iodine with strong nitric acid. In the pure state it is a solid crystalline substance, much more stable than the other oxyhalogen compounds, and is decomposed only on heating into iodine and oxygen. Its salts are much less soluble than the corresponding chlorates, barium iodate being difficultly soluble.

A *periodic acid* is also known. It is crystalline but the crystals have the composition  $\text{HIO}_4 + 2 \text{H}_2\text{O}$  or  $\text{H}_5\text{IO}_6$ . It forms a great variety of salts and is made by the action of strong oxidizing agents on the iodates.

*Oxygen compounds of fluorine* are unknown.

## § 27. AMMONIA.

**200. Ammonia.** — Nitrogen forms with hydrogen the very important compound *ammonia*,  $\text{NH}_3$ . This gaseous substance is best known in the form of its aqueous solution, which under the name *spirits of ammonia* is largely used for household and medicinal purposes. The characteristic, tear-producing smell of the liquid is due to the gas which can easily be obtained by heating the solution. If a few pieces of sodium hydroxide are added, the gas is driven out without heat, so that it can be collected and its properties studied.

Ammonia is a colorless gas which dissolves freely in water and must, therefore, be collected over mercury. If the gas is brought in contact with a little water, it is dissolved almost as energetically, as in the case of the experiment with hydrochloric acid gas. On heating the solution, however, it loses

all of the gas, in contrast to the behavior of aqueous hydrochloric acid. The boiling point of the solution, therefore, is below  $100^{\circ}$ , and boiling begins at the temperature at which the liquid is saturated with gas and slowly rises to  $100^{\circ}$ , the boiling point of pure water. This is because the combination of ammonia with water is less stable than that of water with hydrogen chloride.

Ammonia will not form spontaneously from its elements, but if electric sparks are passed through a mixture of one volume of nitrogen with three of hydrogen, small amounts of ammonia are formed. The reaction soon stops, however, as the ammonia formed is decomposed by the electric discharge. If the experiment is carried out over sulphuric acid it is possible to carry it to completion, because the ammonia is removed from the influence of the spark as soon as it is formed.

If, on the contrary, sparks pass through ammonia gas, it is decomposed almost completely and the volume of the gas is nearly doubled. Therefore, three volumes of hydrogen and one volume of nitrogen combine to form two volumes of ammonia gas.

The volume relations of ammonia to nitrogen gas can be observed by oxidizing the former with bromine in alkaline solution (p. 243). Collect some ammonia gas in a tube over mercury, as was shown on page 208 for hydrochloric acid. Then add a little water by means of a bent pipette (Fig. 68) to show the absorption of the gas by water. Next introduce an alkaline bromine solution in exactly the same way. Nitrogen is evolved with much foaming, and the gas occupies half as much space as before. Enough of the alkaline bromine solution is added to give a permanent color, showing that an excess of hypobromite is present. The decomposition takes place according to the equation

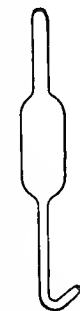
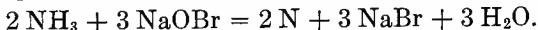


Fig. 68.

Because of its hydrogen content, ammonia ought to be combustible, but it is not easy to cause its combustion even with oxygen. It can be done, however, by generating the gas from concentrated ammonia water in a wide-mouthed flask and then introducing

pure oxygen through a tube pointing downward. The mixture of ammonia and oxygen may then be lighted, but the flame soon shifts to the end of the tube, showing that the oxygen is burning in ammonia. This apparently unusual phenomenon is due to the fact that it is the oxygen and not the combustible gas that is coming from the mouth of the tube. The flame itself always represents simply the space limits between the two acting gases within which mutual action can take place.

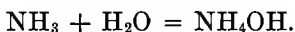
**201. Sources and production.** — Free ammonia occurs in small quantities in the air. This is because the decay of nitrogenous substances ordinarily changes the nitrogen to ammonia. Cow stalls, cesspools, and similar places often smell strongly of ammonia. The ammonia gas generated cannot, of course, go anywhere except into the air, but it is taken from the air by water, so that rain water almost invariably contains ammonia, particularly if a long time has elapsed since a previous rain.

Ammonia is a very important source of combined nitrogen for plants, although, to be sure, they cannot take it up as such but only in the form of nitrates. Cultivated land contains, however, a number of tiny living organisms which under the influence of atmospheric oxygen are able to transform ammonia into nitrates, so that ammonia compounds are almost as good fertilizers as nitrates.

All fossil coals (anthracite coal, bituminous coal, etc.) contain nitrogen, and this on dry distillation is partly changed to ammonia. It will be shown later that in the manufacture of illuminating gas this ammonia collects in the aqueous distillate. It is then separated by distillation from the gas liquors, which contain only a small amount (roughly one per cent) of ammonia. Similar gas liquors are obtained in the making of coke from coal, where not so much the resulting gas but the coke is the principal product; it is used in enormous quantities in the smelting of iron. These are to-day the chief sources of ammonia. There are numerous other substances and mixtures of plant and animal origin, such as, for instance, the waste matter from cities, ocean and lake slime, turf, etc., which on dry distillation give up their combined nitrogen as ammonia. It is necessary for animal

life that a certain amount of nitrogenous food shall undergo a transformation in the body, nitrogen leaving the body regularly in the urine. In this way, for example, about 11 pounds of combined nitrogen pass through a human body annually, and is subsequently converted into ammonia and could be recovered as such.

**202. Ammonium.**— If ammonia water is tested with red litmus paper it is found to react alkaline and must, therefore, contain a hydroxyl compound. On the other hand, gaseous ammonia contains no oxygen and therefore no hydroxyl. The apparent contradiction is explained in much the same way as with sulphur dioxide, sulphur trioxide, etc. When ammonia dissolves in water, it combines with the latter and forms a base according to the equation



There is formed, then, the hydroxyl compound of the group,  $\text{NH}_4$ , which is obviously different from  $\text{NH}_3$ . The new group is called *ammonium*.

The reaction is exactly analogous to the formation of sulphuric acid from sulphur trioxide and water, in which the hydrogen compound of  $\text{SO}_4$  is formed. The latter is the characteristic sulphate group and in salts stands in the same relation to the metals as chlorine does in chlorides, except that in place of an element we find here a group of several elements. In ammonia solution, instead of the metal which usually forms a base with the hydroxyl, we have the  $\text{NH}_4$  group acting toward hydroxyl exactly like a metal. As a component of salts,  $\text{NH}_4$  is called the *ammonium ion*. Free ammonium is not known, though a solution of it in mercury has been obtained and has the same properties as a solution of sodium in mercury. If the solution is kept, it soon decomposes into ammonia and hydrogen in exactly the proportion represented by its formula.

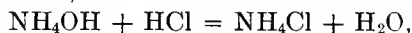
The question next arises as to whether the base can form salts with acids. This is best answered by an experiment. Take some of the ammonia solution, add a few drops of litmus solution and a little hydrochloric acid, and note the result. The liquid becomes hot, indicating that a strong chemical reaction has taken

place. Moreover, we find that whereas the solution was alkaline at the start, the addition of a certain amount of hydrochloric acid makes it neutral. If the neutralized solution is evaporated, a white salt, similar to common salt, is left behind. This salt has a sharp salty taste, is easily soluble in water, and behaves in every way like a salt. It shows one peculiar property, however, inasmuch as on being heated it volatilizes completely without melting. If a small quantity of it is heated in a narrow glass tube, a white sublimate collects on the colder walls of the tube, while the solid in the bottom gradually disappears. This transformation from the solid to the gaseous condition and the reverse without an intermediate molten state is called *sublimation* (p. 67).

The salt described above is called, in accordance with what has been said of it, *chloride of ammonium* or *ammonium chloride*. It is well known under its old name, *sal ammoniac*. It is used in medicine and also in tinning and soldering in which processes it has the property of making the metal more easily wet by molten tin or by molten lead.

Ammonium forms salts with all acids in exactly the same way; all these salts are soluble in water and can be made by neutralization and evaporation.

If we consider the reaction which expresses the formation of ammonium chloride,



we notice that in the process one combining weight of water is liberated, which is exactly the same amount as was used in making ammonium from ammonia. It would, therefore, seem possible, at least according to the formula, to avoid adding water simply to have it withdrawn again, and it might be asked if ammonia would not combine directly with the acid, perhaps in this way:



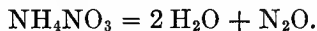
The experiment must naturally be made with ammonia gas, as in aqueous solution water would of course be present. Pour a little strong ammonia into a large beaker and hold over the beaker a glass rod which has been dipped into concentrated hydrochloric acid. We know that ammonia is being given off from the liquid in the beaker and that hydrogen chloride evaporates



from the concentrated acid. The beaker is at once filled with white clouds consisting of ammonium chloride in the form of a very fine dust; it is formed by the union of the two gases. The phenomenon is so striking that it is used as a test for ammonia, and *vice versa*.

**203. Other ammonium salts.** — Ammonium salts of all other acids may be made by neutralizing them with ammonia. Of these, ammonium sulphate,  $(\text{NH}_4)_2\text{SO}_4$ , should be mentioned first. This is prepared in large quantities from the ammonia of the gas works and coke ovens. The gas is expelled from the liquor by heat and is led into concentrated sulphuric acid. The anhydrous salt crystallizes in the orthorhombic system and is very soluble in water. It is used on a large scale as an artificial fertilizer to furnish nitrogen to the soil.

*Ammonium nitrate*,  $\text{NH}_4\text{NO}_3$ , is made from nitric acid and ammonia and forms large, easily soluble crystals which belong to one of four crystal forms, depending on the temperature. On heating it decomposes into water and a gaseous nitrogen compound,  $\text{N}_2\text{O}$ , according to the equation



The compound  $\text{N}_2\text{O}$  is called *nitrous oxide* and behaves quite unlike the other oxides of nitrogen (p. 233). Nitrous oxide does not go over to a higher oxide of nitrogen on contact with air, nor is it decomposed by water, but remains unchanged and is split into nitrogen and oxygen only at comparatively high temperatures. It is also noncorrosive and nonpoisonous to human beings. To be sure, on being inhaled it produces intoxication (it is often called laughing gas) and insensibility to pain, eventually causing unconsciousness. Thus it is used in minor surgical operations, especially by dentists. Since it does not give up its oxygen in the body, it is customary to mix it with oxygen and compress it in steel cylinders.

Ammonium nitrate mixed with carbon or other combustible substances is much used as a safety explosive. Ordinary explosives when used in coal mines are apt to set fire to combustible material of the mine, whereas explosives made from ammonium nitrate will not do this.

## CHAPTER IX.

### CARBON.

#### § 28. CARBON.

**204. Diamond.** — Next to oxygen, carbon may be considered the most important element. It is particularly the element of *living things*, for all organic substances, *i.e.*, the material of which the bodies of animals and plants are made, are compounds of carbon, and the particular properties of these compounds govern those special chemical reactions which are associated with the phenomena of life.

The element carbon has been known in its various forms for a very long time. The most beautiful form is the *diamond*, a mineral occurring in regular crystals, harder than all other minerals, perfectly colorless in the pure state, but showing a brilliant play of colors because of its strong refraction and dispersion of light. For a long time it was not known that the diamond consists entirely of the element carbon, and not until the end of the eighteenth century was it shown to be combustible and to give on combustion exactly the same product and in the same quantities as the other forms of carbon. It can also be changed into the other forms of carbon.

The crystals of diamond belong to the isometric system, the simplest forms of which are the regular octahedron and the cube (p. 187).

In addition to the faces of the octahedron and cube, many other faces are found in the diamond. They are always present in such places and in such numbers as to satisfy the symmetry relations that have been described, so that a diamond may be used to decide whether or not a crystal belongs to the isometric system.

Diamonds are used as ornaments and have a further tech-

nical interest because of their great hardness. They are used for cutting glass, boring stones, and working up hard objects of all kinds (hardened steel for example). For such purposes, diamonds so colored by impurities that they are unsuitable for precious stones are used. There is also known a black form of diamond which is used only for such work. As the diamond is moderately brittle, it can be crushed to a fine powder in spite of its hardness, and may be used in polishing other diamonds.

**205. Graphite.**—Another form of carbon is *graphite*. It is best known through its use in "lead" pencils, which contain no lead at all but are made from graphite which resembles it and which is brought to the desired hardness by the addition of clay and by burning. Graphite is found free in a few localities and appears in the shape of grayish-black masses with somewhat less than metallic luster. It consists of a large number of exceedingly thin leaves and for this reason has a peculiar smoothness. On this characteristic, too, depends the usefulness of graphite as a lubricant for heavy machinery.

Graphite can be prepared artificially by heating any of the forms of carbon to a high temperature. For example, the ends of the carbon rods used in the arc lamps, and between which the electric flame passes, are changed to graphite. Diamond is also changed to graphite when strongly heated. This is, therefore, the form of carbon which is stable at high temperatures. The technical production of graphite is based on this fact, as it is made by heating ordinary carbon with an electric current. The transformation is hastened by the presence of foreign substances, particularly clay.

Graphite is very hard to burn, even more difficult than the diamond. To make it burn in the true sense it must be heated in oxygen. Since graphite can be melted only with the very greatest difficulty, it forms a material exceedingly resistant to heat and is used therefore in preparing crucibles and for other pieces of apparatus that have to withstand high temperatures.

The crystal form of graphite is not definitely known as it forms, for the most part, only in the shape of microscopic plates.

It has been shown, however, that only one crystal form of graphite exists.

**206. Amorphous carbon.** — In addition to graphite and diamond, still another form of carbon exists which is not crystalline but amorphous (p. 199). This is the common charcoal left after subjecting plant or animal matter to a high temperature in the absence of air. If air is accessible, the carbon which all these substances contain is burned and only the non-volatile parts are left behind as ashes. If, on the other hand, the access of air is prevented, the other elements contained in the substance, *i.e.*, the oxygen, hydrogen, and nitrogen, form gaseous compounds which escape, leaving behind the carbon more or less contaminated by the nonvolatile substances which may be present.

As carbon does not melt at this temperature, it is left, in case the organic substance is not liquid, in the shape that the original substance had. So, for example, in wood charcoal the cells of which the live wood was composed may be recognized. Such charcoal is usually fairly impure. Charcoal which because of its method of formation cannot contain nonvolatile substances is much purer, as for instance the lampblack which separates from a chilled flame. This amorphous charcoal is black, and almost all the black colors used in printing, painting, etc., are composed of it. Since lampblack is not appreciably oxidized at ordinary temperatures such colors are extremely durable, particularly as carbon is not attacked by other substances at low temperatures or changed into compounds. Signatures, etc., which are made with carbon will last unchanged for centuries, while those made with common ink (a black iron compound or an organic dyestuff) fade in the course of time. Notices in laboratories or places exposed to chemical vapors should always be written with India ink, made from carbon, rather than with ordinary ink which is destroyed in a few weeks.

At about 400° amorphous carbon unites with the oxygen of the air, forming a gaseous compound which contains two combining weights of oxygen and is called *carbon dioxide*. Exactly the same carbon dioxide is formed when diamond and graphite

are burned, and from 12 parts of diamond, graphite, or amorphous carbon exactly 44 parts of carbon dioxide are obtained, regardless of the form of carbon used. This is a proof that all the forms of carbon consist of the same substance in the chemical sense, *i.e.*, of elementary carbon.

Since ordinary, amorphous carbon, and also diamond, can be changed to graphite by strongly heating, the question arises as to whether the other forms of carbon cannot also be changed to diamond. This has been done, but the diamonds made up to the present time are so small that they can be seen only under the microscope. For the transformation, special conditions are necessary which cannot yet be established on a large scale and which, moreover, are not exactly known. We have as yet no certain knowledge of the way in which diamonds are formed in Nature.

#### § 29. CARBONIC ACID.

**207. Carbon dioxide.** — Carbon dioxide results from the combustion of carbon and of all substances containing carbon; it is a colorless gas forming a regular constituent of the air, as the burning of all carbonaceous material sends the gas into the air. In the pure condition it can be changed by heavy pressure into a liquid which has a pressure of 55 atmospheres at 18°. The liquid comes on the market, compressed in the well-known steel cylinders, under the name *liquid carbonic acid*. It is used in soda fountains in the preparation of carbonated drinks and has many other technical uses. If the liquid is allowed to escape into the air by opening the valve, part of it immediately evaporates and cools the rest to such a low temperature that it hardens to a solid mass like snow. It is best to allow the mixture of gas and solid to empty into a thick cloth bag, which will allow the gas to pass and hold back the solid part. The solid has a very low temperature and is used, therefore, in cooling other substances. For this purpose it is usually mixed with alcohol or ether to make a thin paste, and in this way the temperature may be kept constant at  $-80^{\circ}$  as long as solid carbon dioxide is present.

Carbon dioxide is about one and one-half times as heavy as air and therefore sinks in it, so that vessels can be filled with carbon dioxide by direct displacement of air. If a liter flask is tared and then filled with carbon dioxide, it becomes noticeably heavier (about 0.5 g.). The gas can be poured from one container to another. If a small flame is burning in the second vessel, it will be extinguished, as carbon dioxide cannot support combustion.

**208. Carbonic acid.** — The name *carbonic acid* as applied to carbon dioxide arises from the fact that the latter combines with water to form an acid; but this acid, on its part, readily breaks down again into water and carbon dioxide. The greater the pressure the more soluble is the gas in water. Under one atmosphere of excess pressure, that is, at two atmospheres total pressure, the saturated solution contains twice as much as at atmospheric pressure and the quantity of dissolved gas increases in direct proportion to the pressure. This is a law discovered at the beginning of the nineteenth century by the English physicist, Henry, and holds for all gases which are not too soluble in the liquids. As, in accordance with Boyle's law, the quantities of gases present in equal volumes are proportional to the pressure, it follows that a given quantity of liquid always dissolves the same volume of gas independent of the pressure. If, for example, the pressure is four atmospheres, then four times as much of the gas by weight will dissolve; but this fourfold amount due to the fourfold pressure occupies the same volume as one-fourth as much at one atmosphere pressure.

Aqueous solutions of carbon dioxide, saturated with the gas under a few atmospheres pressure, and often with the addition of other substances, are sold under the name of carbonated waters, soda waters, and tonics. So, too, the natural spring water, formed by rain water filtering down through layers of earth and rock and coming out at some lower spot, usually contains a considerable amount of carbon dioxide. The latter is formed in the earth by the slow oxidation of the vegetable matter present, and the lower the temperature the more freely it dissolves in water. In contrast to solid substances, most of which become more soluble with rising temperature, the solubility of gases

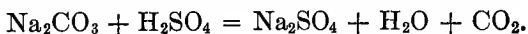
decreases with increasing temperature. And so, the cooler the spring water is, the more carbon dioxide it will contain and the more refreshing its taste.

Carbonic acid present in the aqueous solution of carbon dioxide has the composition  $\text{H}_2\text{CO}_3$  and is formed by a direct combination of the gas with water:  $\text{CO}_2 + \text{H}_2\text{O} = \text{H}_2\text{CO}_3$ . This is exactly analogous to the formation of sulphurous acid from sulphur dioxide and water (p. 200).

Carbonic acid is known only in the form of its aqueous solution, for on evaporation it decomposes into carbon dioxide and water. The composition of the acid, as given in the formula, is based on the composition of its salts. If, for instance, a solution of carbonic acid is treated with sodium hydroxide, the resulting salt can be obtained by evaporation. It has the composition  $\text{Na}_2\text{CO}_3$ , and its formation takes place in accordance with the equation  $\text{H}_2\text{CO}_3 + 2 \text{NaOH} = \text{Na}_2\text{CO}_3 + 2 \text{H}_2\text{O}$  and is found to be the well-known substance *soda*.

A substance formed from another by the loss of the elements of water is called an *anhydride* (p. 194). Carbon dioxide is thus the anhydride of carbonic acid, or, more briefly, it is *carbonic anhydride*. As even this name is long, the name *carbonic acid* is often used instead of carbon dioxide, although this is inexact phraseology.

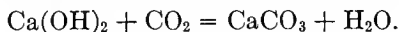
Carbonic acid is a weak acid, for its aqueous solutions do not color litmus solution bright red as do stronger acids, but only a bluish red, and on boiling the carbon dioxide escapes so that the blue color comes back. For this reason almost all acids will decompose the salts of carbonic acid, the carbonates, with an evolution of carbon dioxide and a formation of their own salts. For example, if sodium carbonate is treated with an acid, the solution effervesces and carbon dioxide escapes. If sulphuric acid is used to decompose the carbonate, the equation is



This is the way in which carbonic acid is made in the laboratory, and often commercially as well, *i.e.*, by decomposing a carbonate with an acid. Calcium carbonate has been found

the most practical, for it occurs in large quantities in the earth's crust as limestone or chalk. Sulphuric acid is commonly used in factories and hydrochloric acid in the laboratory. The former forms an insoluble calcium salt and the latter a readily soluble one, so that the generation of gas takes place more easily and regularly in the second case. As the evolution of gas takes place in the cold, the simple form of generator as used in the study of hydrogen (p. 135) may again be employed.

A very sensitive test for carbon dioxide is lime water (p. 219). By the action of carbon dioxide on calcium hydroxide, the corresponding salt, calcium carbonate,  $\text{CaCO}_3$  is formed:



This carbonate is insoluble in water and therefore appears as a white turbidity, giving the lime water a milky appearance.

If clear lime water is exposed to the air, it soon becomes covered with a crust of calcium carbonate, showing the presence of carbon dioxide in the air. If a large beaker is held for a few minutes in the flame from burning alcohol, illuminating gas, oil, petroleum, wood, or other plant substance, and then a little lime water is shaken about in the beaker, a white precipitate forms in each case, indicating that all of the substances have formed carbon dioxide on burning and are, therefore, carbon compounds.

**209. Combustion of carbon.**— Combustion is constantly going on to a very great extent. Not only is practically all the heat used in housekeeping and in the arts produced by the combustion of carbonaceous materials, but the life processes of men and animals are based on the same reaction. This may be shown by blowing air from the lungs through lime water. The solution becomes milky at once, showing that the breath contains a considerable quantity of carbon dioxide which comes from the carbon in the food that is constantly being consumed in the body. In the same way that heat and energy are produced in the technical world, heat and energy are produced inside the human body by combustion, except that in the body cells this process occurs without flame and more slowly than when free combustion takes place. Exactly the same



amount of heat is generated as could be produced by quickly burning the same amount of combustible foodstuff, only it is spread over a much longer interval of time. It is, therefore, necessary that men and animals always have enough free oxygen to supply the amount needed for this combustion. When men and animals are confined in a closed space, the air gradually grows "bad," *i.e.*, it loses its free oxygen, and must be replaced by fresh air if life is to be sustained.

The general need for combustible material and oxygen is not confined to the larger living things but the very smallest beings exist in exactly the same way at the expense of chemical energy. They, too, use up oxygen and compounds containing carbon and generate carbon dioxide. Again, in the process of decay, which is caused by tiny living things, oxygen is used up and carbon dioxide generated. All these quantities of carbon dioxide pass into the air and are mixed with it by the wind, which soon equalizes local differences.

**210. Action of green plants.** — That the ocean of air was not long ago filled with carbon dioxide is due to the fact that in green plants the gas undergoes a decomposition by which free oxygen is formed and returned to the air. The energy necessary to do this is furnished the plants by the sunlight; plants can be effective in this way only when in the light. They then give off free oxygen, and retain the carbon which, when united with hydrogen, a little oxygen and other elements, forms the various materials that constitute the plant. A part of the energy thus bestowed is used by the plants for their own life functions, but another part is stored away and with it they provide not only for their own increase but also for the preservation of all animals and men. The latter get their nourishment either directly from plants or from animals which are in turn herbivorous. We owe our existence, then, chiefly to the sunshine, and plants are the indispensable agents which change the energy of the sun's rays into chemical energy and thus make it available for the maintenance of life. Carbon makes a *cycle through plant and animal life*, acting as a carrier of chemical energy, which it takes up in plants and transmits to animals. Oxygen, however, plays

an equally important part, since the energy can only be utilized by the combination of carbon with oxygen.

While carbon dioxide is, in a way, a food for plants, it is in a certain sense poisonous to animals, inasmuch as they cannot live in an atmosphere that is composed wholly, or to a great degree, of carbon dioxide. It is not a true poison, for it is being constantly formed in the lungs and is regularly exhaled by them; but this removal must be fairly complete or else the absorption of oxygen into the body will be hindered. These processes are completed by the interaction between the inhaled air and the blood; the latter is pumped by the heart into the arteries, which partly carry it to the lungs. The lungs are spongy masses in which a very intimate contact takes place between the air and the blood; here the carbon dioxide, which the blood brings with it from the tissues, where it was formed as the oxidation product of the consumed nourishment, is exchanged for the oxygen of the inhaled air, and this oxygen passes on with the blood to the tissues, there to carry out combustion. The blood, therefore, brings fresh oxygen to the tissues and takes away the consumed oxygen in the form of carbon dioxide. The heart contains a nervous regulator which causes the cycle to take place more quickly, if necessary, when there is, for any reason, an increase in the amount of carbon dioxide in the blood. To this fact is due the increased heartbeat when a more rapid combustion is caused by violent muscular exertion or when, because of sickness, the lungs cannot do their full duty.

Suffocation by carbon dioxide, which can easily occur where the gas is being generated and collected, can be overcome in its first stages by providing as quickly as possible a plentiful supply of oxygen and by the removal of the carbon dioxide. This can be effected by artificial respiration, which consists in a kneading process on the upper part of the body, causing the chest to be compressed and expanded alternately; in this way the lungs are freed of carbon dioxide and filled with fresh air containing oxygen.

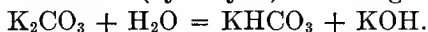
**211. Carbonates.**—Salts of carbonic acid are called *carbonates*. Since carbonic acid is dibasic, there are *normal carbon-*

ates or acid carbonates<sup>1</sup> according to whether both or only one of the hydrogen atoms are replaced by the metal. Because of the large amount of carbonic acid in nature most of the principal metals form carbonates some of which are of great importance in science and in the arts.

Normal carbonates of the alkali metals have been known for centuries as aids in washing and in the manufacture of soap. Potassium carbonate is found in the ashes of wood and other plant substances and can easily be obtained by leaching them with water. While this process was of great importance in earlier times, it has now been completely displaced because it furnishes far too small an amount to meet the tremendous demands of present day industry. Potassium carbonate is made by a process exactly like that used in making sodium carbonate, which will be described later.

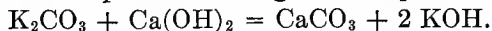
The potassium carbonate made from ashes was called *pot ashes* because the crude salt, colored brown from half-burned plants, was heated in "pots" to burn it white. Such a salt was always impure.

Potassium carbonate is soluble in water and its solutions react alkaline. In aqueous solution it is partly decomposed into free alkali and acid carbonate (hydrolysis) according to the equation



Potassium carbonate, or potash, is much used in the chemical industries, in photography, etc., as a substance of mild basic properties which is decomposed by practically all acids with the formation of the corresponding salt.

**212. Preparation of caustic alkalies.**— On being treated with lime, potassium carbonate undergoes an important transformation whereby calcium carbonate and caustic potash are formed. The reaction takes place according to the equation



A dilute solution of potassium carbonate is heated with milk of lime until a sample of the liquid, after being filtered, gives no effervescence on treatment with an excess of acid. The reaction

<sup>1</sup> The acid salts of carbonic acid are called *bicarbonates* because they contain two equivalents of acid to one of the base.

can be carried out in iron vessels, as they are not attacked by alkali. When the transformation is complete, the precipitated calcium carbonate is allowed to settle and the clear liquid drawn off and evaporated. Potassium hydroxide melts so readily that the solid hydroxide never separates out during the evaporation but the solution changes directly from the solution to the molten alkali. After the water has been expelled, the product is poured into iron drums, in which it hardens and is brought to the market. For laboratory purposes, it is usually purified again and then poured into sticks, as large masses are so tough that they are difficult to break up.

**213. Acid carbonates.** — If carbon dioxide is led into a concentrated solution of potassium carbonate, it is absorbed freely and crystals of the acid carbonate are formed according to the equation 
$$\text{K}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O} = 2 \text{KHCO}_3.$$

Potassium acid carbonate, or potassium bicarbonate, is much less soluble than the normal salt, and by precipitation with carbon dioxide the pure bicarbonate can be made from an impure carbonate, as the impurities will stay in the mother liquor. When the salt is heated, half of the carbonic acid is driven off and the normal carbonate is again formed. The equation corresponding is the opposite of that just given. The reaction reverses at a high temperature because the water and carbon dioxide are both gaseous under these conditions and so are removed from the field of action. Even though the decomposition is very slight at first, it must keep on because the decomposition products are volatilized and thus the equilibrium is disturbed. The reaction goes in the reverse direction in the solution, as the bicarbonate formed separates out in the solid form and in that way overthrows the equilibrium. If the bicarbonate is heated under a heavy pressure, so that the gases cannot escape, it is not decomposed.

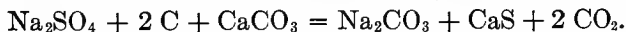
**214. Soda.** — The carbonates of sodium are exactly similar to those of potassium. The normal carbonate,  $\text{Na}_2\text{CO}_3$ , is called *soda*<sup>1</sup> and, like potash, has been known since early times. It is

<sup>1</sup> The beginner should be careful not to confuse *caustic soda*,  $\text{NaOH}$ ; *baking soda*,  $\text{NaHCO}_3$ ; and ordinary *soda*,  $\text{Na}_2\text{CO}_3$ , which is sometimes called *washing soda*.

found in the ashes of some aquatic plants and is also formed in the salt lands of Egypt. At first no distinction was made between it and potash, which it strongly resembles, and it was not until the seventeenth century that people began to distinguish between the "vegetable alkali" (potassium hydroxide) and the "mineral alkali" (sodium hydroxide), after it was discovered that they gave different salts. At the end of the eighteenth century, Klaproth, a Berlin chemist, discovered that the "vegetable alkali," which up to that time had been made entirely from plant ashes, also occurred in many minerals, and since that date the present names have been used.

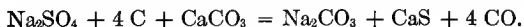
Soda, or sodium carbonate, is made to-day in enormous quantities from common salt, as in this case, too, the natural supply is insignificant in comparison to the demand. There are two principal processes of manufacture.

The older method originated when, at the end of the eighteenth century, the French republic was at war with almost all of the older European nations and all the potash that the land produced was used in making saltpeter for the powder mills. A prize was offered, therefore, for a process which would return to the industries the alkali that had been taken away, and the method of Le Blanc, which won the prize, was chiefly used for almost a century. It consists of the following operations. Common salt is first treated with sulphuric acid, forming sodium sulphate and liberating hydrochloric acid as a by-product. We already know the reaction (p. 207). The sodium sulphate is heated with calcium carbonate and carbon, whereby the sulphate is reduced to sulphide, and the latter reacts with calcium carbonate to form sodium carbonate and calcium sulphide,



The resulting carbon dioxide escapes as a gas.<sup>1</sup> From the solid mixture of sodium carbonate and calcium sulphide the former is extracted by water, in which the sulphide is not very soluble. The method of counter currents naturally comes into

<sup>1</sup> When the reaction nears completion, carbon monoxide (p. 269) is also formed:

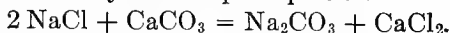


use again, and the nearly exhausted residue is treated with fresh water, while the fresh mass comes in contact with a nearly saturated solution. The water and the crude mass thus move in opposite directions and finally separate as a saturated solution on the one hand and a leached-out residue on the other. On cooling the warm saturated solution, soda crystallizes in large crystals containing  $10 \text{ H}_2\text{O}$ ; in other words, the so-called *soda crystals* are  $\text{Na}_2\text{CO}_3 + 10 \text{ H}_2\text{O}$ .

**215. The Solvay process.** — The method described above is used less and less, as it does not give a pure product. Soda is now made largely according to the plan of the Belgian, Solvay. This process depends on quite different reactions and, unlike the other method, is carried out in the wet way. An aqueous solution of common salt is treated under pressure with ammonia and carbon dioxide. Sodium bicarbonate separates as the most insoluble product and ammonium chloride is left in the solution. The reaction is as follows:



The bicarbonate (which is similar to the corresponding potassium salt) is separated by filtration. The ammonium chloride is changed into ammonia and calcium chloride by heating with lime,  $2 \text{ NH}_4\text{Cl} + \text{CaO} = \text{CaCl}_2 + 2 \text{ NH}_3 + \text{H}_2\text{O}$ . This brings the ammonia back into the process again: The sodium carbonate is formed by gently heating the sodium bicarbonate and the liberated carbonic acid is returned to the process. This is, of course, only half the amount needed for the production of the same quantity of carbonate, the other half being liberated in the burning of the lime used in decomposing the ammonium chloride. If the ammonia, which is really not used up in the process, is left out of consideration, the process of manufacture may be represented by the simple equation



Since the process indicated by this equation will not go of its own accord (on the contrary calcium chloride and sodium carbonate react directly to form sodium chloride and calcium carbonate), the indirect method involving ammonia is necessary to get the desired results.

Sodium carbonate crystallizes, as already stated, with 10 H<sub>2</sub>O in large crystals which weather easily and melt at 37° to a liquid in which a solid salt with 1 H<sub>2</sub>O separates. All of the water of crystallization goes off on moderate heating, and even on standing in the air the soda crystals change into a white powder. The soda made by the second process is of course anhydrous. When the anhydrous salt is treated with cold water, in an attempt to dissolve it, the hydrated crystals form very easily and the mass hardens to a solid cake which is not very soluble. The trouble may be overcome by stirring the anhydrous salt or by dissolving it in water heated to 30° to 40°.

Soda has an extended use in the arts. Its solutions behave in most respects like those of potassium carbonate, and like the latter it reacts alkaline because of hydrolysis (p. 259).

Soda is changed to *bicarbonate of soda* by the action of carbon dioxide and water. This salt is much used in medicine as a mild alkali. It is also used in the manufacture of Seidlitz powders. These consist of equivalent quantities of sodium bicarbonate and *cream of tartar*, an acid potassium salt occurring in grapes. When the two powders are dissolved in water separately, and the resulting solutions mixed, carbon dioxide is generated, part of which is evolved as a gas while the rest stays in solution. The mixture is not unpleasant to drink, and the sodium potassium tartrate formed (Rochelle salt) acts as a laxative.

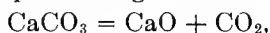
**216. Calcium carbonate.** — The carbonates of calcium and magnesium are also important substances. Both occur in enormous deposits which have been formed in the earth's crust by the action of carbonic acid and water on the rocks originally present. Carbonic acid has thus combined with the alkaline earth metals and formed layers of carbonate, at first on the sea bottom. These strata have in some cases been changed into mountains by later geological upheavals, and in other cases have been left in their original horizontal positions, though no longer covered with water. Later geological processes have changed the forms of these deposits very materially.

Natural calcium carbonate in its purest form is called *calcite* and is a colorless mineral which crystallizes in rhombohedrons

having a ternary axis of symmetry (Fig. 67). The purest crystals come from Iceland (Iceland spar), are transparent like glass, and as they cause objects seen through them to appear double, the mineral is sometimes called "double spar." This property of double refraction arises from the fact that in all crystals which do not belong to the isometric system, every light ray is in general separated into two rays which take different paths and so give different images. Double refraction is particularly marked in double spar and because of the transparency of the mineral is easy to observe.

Ordinary calcite is usually translucent, because of inclosures which do not allow it to crystallize perfectly. If the crystals are small and form a coherent mass, the mineral is called marble. This is white when pure, but is often colored by impurities. Black marble is colored by carbon.

Still smaller, and only made visible to the eye by the glitter of the broken surfaces, are the crystals of ordinary limestone, the most widely distributed form of calcium carbonate. Limestone is used for building purposes and also in making lime by burning. The reaction is a simple cleavage into carbon dioxide and lime,



and takes place at a white heat (p. 265).

Other forms of natural carbonate are chalk and aragonite. The former is made from the remains of tiny living organisms, which built shelters for themselves, as is done to-day by thousands of the lower animals (mussels, snails, etc.). Chalk is fairly free from organic compounds, and forms mountains which, when they happen to lie on the seacoast, are ground off to steep cliffs. Chalk is a soft, white, amorphous substance, easily changed to a fine powder, and is used for whitewashing, writing,<sup>1</sup> and other purposes.

Aragonite is a mineral of rather uncommon occurrence and is chiefly of interest as a polymorphic form of calcium carbonate, for it is orthorhombic (with three perpendicular binary axes) and not rhombohedral (with one ternary axis) as is calcite. Its

<sup>1</sup> Much of the modern blackboard crayon is made of calcium sulphate, and is really not chalk at all.



density is less than that of calcite, but on gentle heating the crystals of aragonite break down, forming a coarse powder having all the properties of calcite. These last crystals are known as *pseudomorphs*, and are formed when the original crystals of a substance are changed by chemical or other influences into a different substance, the transformation going on so slowly that the original form is preserved. As aragonite is never found in the characteristic form of calcite, whereas calcite is found in the aragonite form, this furnishes another proof that calcite is the more stable form.

Calcium carbonate is formed artificially as a white precipitate whenever the solution of a calcium salt is mixed with a soluble carbonate. The precipitate is at first amorphous and slightly soluble in water. If the wet mass is allowed to stand, it changes to a sandy powder which the microscope shows to be composed of tiny rhombohedrons of calcite. If the precipitation is carried out in hot solution, minute aragonite crystals are formed. The two crystal forms are not appreciably soluble in water. Calcium carbonate, like other insoluble carbonates, is soluble in acids, even the very weak ones, if the acid is capable of forming a soluble calcium salt. This is due to the fact that not only is carbonic acid a very weak acid but it breaks down into water and carbon dioxide which escapes, because of its gaseous form, so that any reactions which tend to form it are aided thereby.

**217. Lime burning.**—When calcium carbonate is strongly heated, it decomposes into lime and carbon dioxide. This operation, "lime burning," is one of the oldest known chemical industries, and the reactions which occur have interested the chemist from earliest times. Since caustic lime is made from neutral limestone, the early belief was that "fire substance" was added to produce the effect. This conception was further developed by the belief that when "mild" alkalies, that is the carbonates, were boiled with lime, the "fire substance" of the latter was transferred to them so that they too became caustic. It was not until about the end of the eighteenth century that Black discovered the reverse to be true. Nothing is added to limestone on burning, but it loses something, *i.e.* carbon dioxide, and this

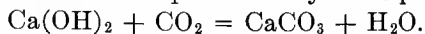
is, moreover, the reason for the behavior of the mild alkalies; they do not take up *fire substance* when lime causes them to become caustic but give up their carbonic acid.

In the latter half of the nineteenth century Deville, in Paris, made the further discovery that limestone when burned behaves very much as water does when boiled. Each temperature corresponds to a definite pressure of carbon dioxide, and the reaction stops when this pressure is reached. It is important, therefore, in burning limestone to remove the carbon dioxide as completely as possible.

Lime burning is carried on in large furnaces or kilns differing in construction according to their location and the conditions under which they work. They sometimes work *continuously* and sometimes *intermittently*. In the latter case the kiln is filled with layers of limestone and brought to the required temperature by burning fuel. After the carbon dioxide is driven off the contents are allowed to cool, taken out, and the kiln refilled. In the case of a continuous kiln, however, the arrangement is such that the burned lime is constantly being removed from the heated section and being replaced by fresh limestone. By this arrangement it is possible to take advantage of the heat of the burned lime, causing it to warm up the cold limestone, and, by arranging such a countercurrent, the best possible utilization of the heat is made. A continuous operation is always fundamentally better than an intermittent one, as it is only with the former that the principle of countercurrents can be used. Intermittent operation, on the other hand, requires a less complicated apparatus and is therefore found as the first stage of every process.

**218. Mortar.** — The properties and reactions of quicklime have already been described (p. 218). Its most important use is in the making of mortar, the hardening of which is based upon the reversal of the reaction which has just been considered. Mortar is composed of calcium hydroxide mixed with an excess of water and a mechanical addition of either sand or powdered limestone. In the form of paste it is put between the stones to be joined and after a time hardens to a solid mass. The chemistry of the process is that the carbon dioxide of the air

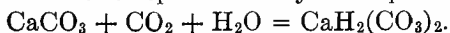
changes the calcium hydroxide into calcium carbonate. Individual carbonate crystals resulting from the reaction grow together and, because of the solubility of the hydroxide, extend into the pores of the stone and form in this way a solid joint. The sand serves to make the mass more porous and is necessary because the hydroxide expands somewhat on changing to the carbonate, so that pure mortar would crack because of the expansion. The reaction is represented by the equation



Water is therefore formed when mortar hardens. That is the reason that freshly plastered house walls are damp if the rooms are occupied, as the carbon dioxide of the breath causes the formation of more water than can be evaporated. To hasten the operation as much as possible, stoves are sometimes set up in the plastered rooms and the products of combustion, rich in carbon dioxide, are not led away but kept inside. This carbon dioxide and the heat both hasten the formation of carbonate in the mortar. Hardening is almost never complete on the interior of walls, and even very old mortar broken out from a wall shows an alkaline reaction on the surface of the break.

**219. Calcium bicarbonate.**— When carbon dioxide is led into lime water a white precipitate of normal carbonate is formed. If the gas current is continued, the solution becomes noticeably clearer, due to the disappearance of a great part of the precipitate. The solution now contains a calcium salt, for if it is heated after filtering, it becomes turbid and carbon dioxide escapes. The white precipitate is found to be normal calcium carbonate.

This phenomenon is due to the fact that the excess of carbon dioxide has formed calcium bicarbonate, which is soluble in water. In this respect, then, the alkalis and alkaline earths behave in exactly opposite ways. In the former the normal salts are more soluble, while in the case of the alkaline earths the acid salts dissolve more readily. This is also true of magnesium and of the other allied elements. On heating, the same decomposition occurs as with the alkali salts. The dissolving of calcium carbonate is represented by the equation



The formula of the bicarbonate is based on the fact that calcium is bivalent and that, therefore, two combining weights of carbonic acid must be taken if only one hydrogen is replaced in each.

The equation read backwards shows the reaction on heating.

These phenomena are of great importance in determining the geological movement of calcium. When rocks containing calcium are decomposed by water and carbonic acid, the calcium carbonate will at first stay where it is formed unless carried away mechanically. But when water containing carbonic acid comes in contact with the normal carbonate, a corresponding amount is changed to bicarbonate and is carried away by the water in solution. For this reason spring water and other natural carbonated waters contain some dissolved calcium bicarbonate, which deposits when the carbon dioxide can escape into the air or when it is used up in other ways. Most limestone deposits are formed in this way, and frequently organisms found in the sea play an important part in the formation, as dissolved limestone is especially useful in building up their shells and hard parts.

**220. Magnesium carbonate.** — Magnesium carbonate, as it occurs in nature, is called *magnesite*, and, like calcite, crystallizes in rhombohedrons. Calcite and magnesite have the same crystal form, or are *isomorphous*. Magnesite is sometimes called *bitter spar* because magnesium sulphate has the name *bitter salt*, and for the same reason magnesium oxide was formerly called *bitter earth*. Magnesite is found in large masses, but not so abundantly as limestone.

An isomorphous mixture of equal stoichiometrical quantities of calcium carbonate and magnesium carbonates forms extensive mountain ranges. The mineral is represented by the formula  $\text{CaCO}_3 + \text{MgCO}_3$  and is called *dolomite*. Weathering makes the rock take on exceedingly complex and unusual forms, so that dolomite mountains are easily recognized.

If a solution of magnesium salt is precipitated with a carbonate, it is not alone the normal carbonate that forms but rather a varying mixture of carbonate and hydroxide, the amount of

the latter being greater the hotter and more dilute the solution. This is because the magnesium carbonate, when formed in solution, undergoes a more or less complete hydrolysis, with the formation of magnesium hydroxide. The latter compound is also insoluble and is precipitated with the carbonate. The dried precipitate is a white, very light powder and is used in medicine under the name *magnesia alba*. It loses carbon dioxide and water very easily when heated, leaving behind magnesium oxide or *magnesia*, which because of its method of formation is known in the drug stores as *magnesia usta*, or "burned magnesia."

**221. Carbon monoxide.** — In addition to carbon dioxide there is another compound of carbon and oxygen which differs from carbon dioxide in being combustible. It contains only half as much oxygen and is therefore called *carbon monoxide*. It has the composition CO and will burn because it can combine with as much more oxygen as it already contains, forming carbon dioxide.

Carbon monoxide is formed by the combustion of carbon at high temperatures, when the carbon dioxide first formed is allowed to stay in contact with hot carbon. Carbon then burns to carbon monoxide according to the equation  $\text{CO}_2 + \text{C} = 2 \text{CO}$ . This reaction proceeds without flame, and will not take place of itself, because it uses up heat instead of generating it. The reaction will go, therefore, only at a high temperature when the heat needed is furnished from the outside.

The formation and combustion of carbon monoxide in stoves, furnaces, etc., can often be noticed, particularly toward the end of the combustion, after the fuel has lost the hydrogen which it contained at first and only glowing coals are left. The natural fossil fuels, anthracite coal, bituminous coal, etc., are not composed of pure carbon, but contain as well varying amounts of hydrogen; soft coal the most and anthracite least. Just as was mentioned in connection with hydrogen sulphide, it is true here that hydrogen burns much more quickly than carbon, so that if a flame is chilled in which both are burning, soot is deposited while the hydrogen still burns. When coal is burned there is formed first a large luminous flame, due chiefly to the burning of

hydrogen (with a little carbon), and there is left a more or less hydrogen-free coal, called coke. In the second period of combustion this coke oxidizes, with a formation of carbon dioxide at the grate where the air enters. This is reduced to carbon monoxide by the glowing layers above the grate, but at the very top, where a free supply of air is available, the carbon monoxide burns to dioxide again. The flame of the carbon monoxide is readily recognized by its blue color, whereas the hydrocarbon flames are yellow, or white, and luminous. The blue of carbon monoxide is much purer and more decided in color than the blue of the hydrogen flame.

Carbon monoxide is a dangerous poison, more dangerous as it is absolutely odorless and therefore only makes its presence known when its poisonous action has begun. It is formed, as described above, when carbon burns with an insufficient supply of air and is made, for example, if after a fire has burned low the flue damper is closed. Every year accidents happen in which whole families are poisoned by the presence of carbon monoxide which gets into the air of the room exactly as stated above.<sup>1</sup> The poisonous action is due to a union of carbon monoxide with the red blood corpuscles. These latter have the function of taking up the oxygen which comes into the lungs in the air breathed, transferring it to the body cells and thus causing the combustion of the foodstuffs in such a way as to furnish the amount of energy necessary to life. By their union with carbon monoxide the blood corpuscles are made permanently unfit to take up oxygen. We are dealing in this case not simply with a lack of oxygen, as in the case of carbon dioxide, but with a process exactly equivalent to a real loss of blood and, therefore, much more difficult to overcome.

Pure carbon monoxide can be made by decomposing formic acid with concentrated sulphuric acid. Formic acid has the composition  $\text{HCO}_2\text{H}$ , and when the elements of water are taken away carbon monoxide,  $\text{CO}$ , is left. By the action of sulphuric acid on a salt of formic acid the free acid is first liberated. Concentrated sulphuric acid then acts to remove water from the

<sup>1</sup> A stove also "throws gas" if the fire is checked too soon after adding fresh coal.

formic acid, leaving carbon monoxide, which can be collected over water in the usual way. The density of the gas is almost exactly the same as that of air and it is only very slightly soluble in water. It can be liquefied by cooling and pressure, but only with great difficulty.

**222. Carbon disulphide.** — Carbon combines with sulphur to form a compound which we have already used (p. 78) as a solvent for sulphur. Carbon disulphide,  $CS_2$ , is obtained by leading sulphur vapors over heated carbon. A union of the two elements takes place with a slight consumption of heat, so that it can only be carried out by constantly supplying some heat from the outside. The reaction product must be strongly cooled, however, as carbon disulphide is very volatile. A part of the sulphur usually stays uncombined and can easily be separated by distillation.

Carbon disulphide has the composition  $CS_2$ , is colorless when pure, but usually is a somewhat yellowish liquid of very high refractive and dispersive power so that when viewed under suitable illumination it shows the colors of the spectrum. It boils at  $46^\circ$ , and, as the vapor takes fire very easily (for instance when touched with an iron rod heated below redness), it must be handled with great care. Pure carbon disulphide is almost odorless; the ordinary preparation, however, contains small amounts of badly-smelling impurities which are difficult to remove. Its density in the liquid condition is 1.27, so that it sinks in water and for this reason is often kept in water, in which it is but slightly soluble. On being burned, it forms carbon dioxide and sulphur dioxide. The vapor is almost three times as heavy as air.

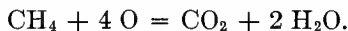
Carbon disulphide is a good solvent for fats and waxes, iodine, bromine, and many other substances insoluble in water. We have learned already that sulphur dissolves in it. It has been used technically as a solvent in many cases and also in the manufacture of certain chemicals, as it readily undergoes a number of transformations. It has been found to act as a poison for some of the lower forms of animal life, and one of its important uses is as an insecticide.

It should be noticed that the formula of carbon disulphide,  $CS_2$ , is like that of carbon dioxide,  $CO_2$ , with sulphur taking the place of oxygen. Similar analogies in the composition of corresponding oxygen and sulphur compounds are frequent, showing to this extent the relation of sulphur to oxygen.

### § 30. HYDROCARBONS.

**223. Marsh gas.** — Carbon forms with hydrogen a large number of important compounds. The simplest of them is a gas of the composition indicated by the formula  $CH_4$ . It has been found in various places and, since it was not known at first that the substance was always the same, was given various names. It forms wherever vegetable matter decomposes in the absence of air, for example in marshes and pools containing dead leaves. If the slime on the bottom is stirred up, gas bubbles rise to the surface and can be collected by means of a funnel in an inverted flask which is filled with water. The gas thus collected contains besides carbon dioxide and nitrogen, a combustible gas called *marsh gas* because of its origin.

The same gas often forms in coal mines and is then called *fire damp*. It is usually found in cavities or bubbles in the coal, and streams out when a "pocket" is opened. When the air pressure goes down suddenly, the gas that has collected in the half-open cracks of the bedrock and of the coal escapes into the galleries and shafts, making a source of great danger to the miners. For, since  $CH_4$  is composed of two combustible elements, it is itself combustible and makes with air an explosive mixture which is exceedingly dangerous. The burning takes place according to the equation



Fire damp, or mine gas, therefore, uses up a large amount of oxygen and forms an inflammable, explosive mixture with a comparatively small amount of air. Even though the lamps used in mines are so arranged that they will not cause explosions, these explosions happen occasionally because of carelessness of the workmen. A mixture of coal dust and air is also dangerous and is the cause of many mine explosions.



A third name for the substance, and the scientific one, is *methane*, derived from the name of *methyl alcohol* from which substance it can be prepared.

**224. Illuminating gas.** — Methane is a constituent of ordinary illuminating gas, made by heating coal rich in hydrogen (gas coal). Coal is heated in large tubular retorts, whereby there results an evolution of gases and vapors of very complex character. The vapors are condensed by cooling and separate into a watery liquid, *gas liquor*, and a greasy or waxy substance, *coal tar*. The gas liquor contains the valuable constituent ammonia (p. 246). Coal tar is composed of many different carbon compounds which in the last forty years have given rise to an important industry as they can be used in preparing dyestuffs, medicines, and other valuable materials. In fact, the chemistry of the carbon compounds is so important that this field of chemistry is usually studied by itself under the name *organic chemistry*. The most important of these compounds contain hydrogen and oxygen in addition to carbon; sulphur, chlorine, nitrogen, and similar elements are sometimes found, however. Metals, on the other hand, occur much less frequently in organic compounds, so that the field of chemistry which pertains to the *inorganic substances*, or those without carbon, is, for the most part, the chemistry of the metals and their compounds.

The treatment of coal by heat alone, without the addition of a liquid, is called *dry distillation*, as the coal itself is dry, even though it gives a liquid on distillation. The gaseous part is a mixture of hydrogen, carbon monoxide, methane, and several other compounds of carbon and hydrogen to be studied later. The gas is treated in special apparatus to free it from volatile sulphur compounds that are formed from the sulphur in the coal, because these compounds not only smell badly but on combustion produce sulphur dioxide, a gas injurious to human beings and to plants. The purified gas is finally collected in large floating cylinders, *gasometers*, from which it is distributed by a system of pipes.

Coal gas is much used for lighting. Formerly only an open flame of burning gas was used, so that in order to furnish the necessary illumination the latter had to contain a definite

amount of compounds rich in carbon. To-day gas burners are usually provided with a "mantle"; the latter consists of a tissue of highly infusible metallic oxides which can be heated white hot by a suitable flame. There is no advantage in having the gas used in heating the mantle self-luminous, but it must be as hot as possible. At the present time, therefore, self-luminous gas is being replaced to a greater and greater degree by a gas giving a hotter flame. Such a gas is also more suitable for heating purposes and for gas engines.

225. **The flame.** — An ordinary flame deposits soot when brought in contact with a cold object. This is because hydrogen burns more quickly than carbon. When, therefore, a hydrocarbon burns, carbon may separate out in the flame; it is then heated to incandescence, and produces light, and possibly smoke. If it is desirable to prevent the formation of free carbon, as for instance in the use of illuminating gas for heating purposes, the burner devised by the German chemist, Robert Bunsen, is used; the burner is based on the principle of mixing a large amount of air with the gas before burning it. The oxygen is sufficient to change the carbon to carbon dioxide, so that the formation of smoke is prevented and the flame loses its illuminating power.

This is accomplished by allowing the gas to come through a small opening into a larger space to which air has access. The stream of gas sucks in air and is so mixed with it that it burns with a colorless, hot flame. The ordinary type of Bunsen burner as used in the laboratory, Fig. 69, is made of an upright exit tube above which is fastened a metal tube about 10 cm. long, having at the base an air inlet that can be made larger or smaller as needed.

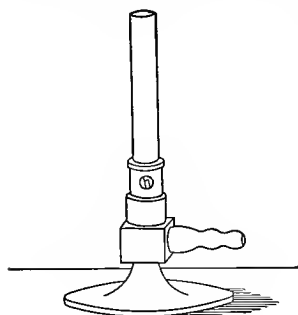


Fig. 69.

If too much air is mixed with the gas, the flame "strikes back," *i.e.*, it burns at the base instead of at the mouth of the tube. This is because too much air forms an explosive gas mixture and the

explosion sets fire to the gas at its exit tube. When this happens in a burner, the flame should be extinguished and the supply of air reduced. In this way a noisy flame is obtained in which tiny explosions of the gas mixture are taking place, but the explosions do not now reach the base of the burner. The flame then consists of an almost green inner cone, in which there is an incomplete combustion of the mixture of gas and air (this inner cone is the coldest part of the flame) and a blue outer mantle where complete combustion takes place with the aid of the outer air. The hottest part of such a flame is just above the inner cone. If the supply of air is still further limited, the flame becomes quiet, because no more explosions take place, and a luminous tip appears on the inner cone, indicating that carbon is beginning to separate out. If objects injured by hot carbon are to be heated, *e.g.*, a platinum crucible, the luminous tip must be avoided and the noisy flame used, which is also hotter. On the other hand, the flame with a smaller air supply is used for work in which too high a temperature is not desirable, as in making glass apparatus for example.

The Bunsen burner is made in a number of different shapes, but all of them have the same fundamental idea of mixing the gas with air. Thus in the Fletcher burner, Fig. 70, the gas outlet tube and combustion pipes are horizontal and lead into a ring-

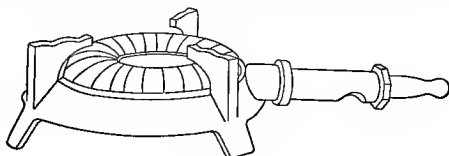


Fig. 70.

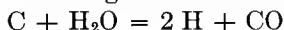
shaped arrangement through which the flame is spread out and divided into numerous small flames. This form is used for heating larger surfaces, as kettles, large evaporating dishes, etc.

A Bunsen burner is also used in incandescent gas lighting. For this purpose a hot flame is needed which is shaped like the mantle and which fills it as exactly as possible and thus heats it uniformly.

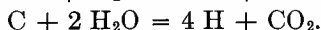
The gas outlet tube is bored with numerous small holes, and the short combustion tube is covered with wire gauze to provide a more complete mixing of the air and gas, and at the same time to prevent a striking back.

As the incandescent burner, using a flame that is originally nonluminous, gives a great deal more light for the same amount of gas than the common fishtail burner does with a luminous flame, it is possible to replace illuminating gas by a nonluminous gas that is also much cheaper to make.

**226. Water gas.** — This is made by bringing steam in contact with hot coal. The following reactions take place:



and



Whether the first reaction preponderates with the formation of hydrogen and carbon monoxide, or the second with a double amount of hydrogen but mixed with carbon dioxide, depends largely on the temperature. The higher the temperature the greater the tendency for the first reaction.

Since a considerable amount of heat is used up in either reaction this must be furnished in some way. It is usually done by first passing a current of air over the coal, causing it to burn and to become very hot. The air supply is then shut off and steam introduced while at the same time the gases evolved are collected. The combustion of the carbon in the water vapor goes on as described according to the first reaction, and later, when the temperature has fallen somewhat, the second reaction takes place. When the temperature has fallen so low that the reaction goes too slowly, the current of steam is stopped and the coal is again heated in air, after which another period of gas formation occurs. By replacing the burned-out coal at regular intervals the series of operations can be continued indefinitely.

Such a gas is called *water gas* from its method of production. It is much cheaper to make than illuminating gas and, because of its high hydrogen content, has a high heating power. Its disadvantage is that it contains carbon monoxide, which is particularly dangerous because water gas is odorless and an accidental leak is not easily detected. If a luminous flame is

needed, hydrocarbon compounds are distilled into the gas, or else it is heated with petroleum residues and in this way some odor is imparted to the gas. At present a mixture of coal gas and water gas is frequently used, but the chances are that in the near future the latter will be used by itself to a very large extent.

**227. Homologous series.**—The removal of one combining weight of hydrogen from water leaves the hydroxyl group; this occurs in all compounds that are made from water by the replacement of one combining weight of hydrogen by another element (for instance a metal). Similarly, the removal of one combining weight of hydrogen from methane,  $\text{CH}_4$ , leaves the group  $\text{CH}_3$  which is found in many organic compounds and is called the *methyl* group. It is obviously univalent because it is formed from a saturated compound by the loss of one combining weight of hydrogen. There are no known compounds of carbon in which for one combining weight of carbon there are more than four combining weights of hydrogen, chlorine, or any other univalent element. Methane, therefore, is called a *saturated hydrocarbon*.

If we imagine one combining weight of hydrogen in methane to be replaced by a univalent methyl group, the result is a substance of the symbol  $\text{CH}_3 \cdot \text{CH}_3$  or a "methylated methyl." Such a compound, having the symbol  $\text{C}_2\text{H}_6$ , is known, but is called ethane. This can be made artificially by means of a reaction in which the methyl group is substituted for an atom of hydrogen in methane, and is found to agree in all its properties with a gas which occurs in natural gas and is often found in oil districts. It has about the same density as air, is more easily liquefied than methane but otherwise possesses much the same characteristics. One of the six combining weights of ethane can in its turn be replaced by a methyl group, forming a compound  $\text{C}_3\text{H}_8$ . This when subjected to the same treatment forms  $\text{C}_4\text{H}_{10}$ , which in turn may be changed to  $\text{C}_5\text{H}_{12}$ ,  $\text{C}_6\text{H}_{14}$ , etc. All of these substances differ in composition by a  $\text{CH}_2$  as each time hydrogen goes out a  $\text{CH}_3$  takes its place. Similar substances are found in American petroleum,  $\text{C}_3\text{H}_8$  being liquid at ordinary temperatures

though it boils at  $17^{\circ}$ . The higher members of the series are colorless liquids, the boiling points of which increase regularly with increasing carbon content.

There are a great many series of similar substances, of which the compositions differ, each from the next below, by one  $\text{CH}_2$  and the properties of which change uniformly with the composition. We can imagine their formation by assuming that in the simplest member one hydrogen is replaced by a methyl group and that the same reaction is repeatedly carried out, as may actually be done in a great many cases. Such a series is called a *homologous series*. A series of this type is very useful in making a study of organic compounds, and helps in the knowledge of the properties of these compounds because similarities and regular changes in properties always exist in any homologous series.

**228. The paraffins.** — The members of the series derived from methane are called the *saturated hydrocarbons* for the reason given above. The first members are colorless gases which at low temperatures change to very mobile liquids, while the higher members have increasingly higher boiling points. Between the fifth and the eighth or ninth members, the liquids are called *petroleum-ether*, *benzin*,<sup>1</sup> *gasolin*, *naphtha*, etc., and because they are good solvents for oils and fats are used technically for fat extraction and also for removing grease spots from clothing. Because of their low boiling point they can be evaporated easily and quickly. They are combustible and the vapor also takes fire easily. This is the reason that gasolin is used in explosive engines and has become of great importance in the automobile business. Pure gasolin has almost no odor, but the commercial article commonly has small amounts of foreign matter which give it a bad smell.

The saturated hydrocarbons beyond the tenth member are found in American petroleum (other petroleums belong to a different series), of which the properties are well known. The higher

<sup>1</sup> Benzin must not be confused with benzene. The former is a mixture of liquid paraffins and the latter a pure substance,  $\text{C}_6\text{H}_6$ , obtained from coal tar.

the position in the series, the lower the mobility and the higher the boiling point of the hydrocarbon.

Still higher in the series come colorless oils not suitable for burning in lamps and called *paraffin oils*. Higher members are of a salve-like consistency and as *vaselin* are used for medicinal purposes and as lubricants. Finally come the wax-like solids of increasingly higher melting point called *paraffins*. The series of saturated hydrocarbons is known as the paraffin series, from the higher members, which have been known for a long time. The name *paraffin* was given because these substances are very inactive chemically; in fact almost all corrosive or otherwise reactive bodies may be brought in contact with them without causing any change. This property is taken advantage of in making dishes of paper and wood waterproof, and impervious to acids and bases, by soaking them in melted paraffin. The low melting point of paraffin unfortunately prevents its use for similar purposes at a higher temperature.

All of these substances occur in crude petroleum, which is found in the earth in Pennsylvania and in other parts of the United States and which looks like brown tar. The various liquid and solid products are obtained by successive distillations and purifications with sulphuric acid. All are mixtures, or rather solutions, of a series of similar homologous compounds. It is difficult to separate the individual members completely, and for most purposes it is immaterial whether several homologues are together or not, as their properties are very similar. Large quantities of the heavy hydrocarbons and paraffins are obtained from the distillation products of bituminous coal.

The series of saturated hydrocarbons called paraffins can be regarded theoretically as the mother substances of a very large and important group of organic compounds called the *aliphatic series*. The name is derived from the Greek word for "fat," and was originally applied to the fats and allied substances. To-day the fats are still classed among the aliphatic compounds, although they are by no means the most important members of the group, nor are they typical. Thus the name has entirely lost its original significance. The aliphatic compounds are all

so related to the hydrocarbons that they can be prepared from them by substituting other elements or groups for one or more of the hydrogen atoms. Then, according to the nature of the substituted groups, widely different classes of other compounds are derived.

**229. Alcohols.** — The hydrogen of all hydrocarbons may be replaced by other elements or groups and thus an almost countless number of the most widely differing compounds are formed. Only a few of these can be described. Among the most important are compounds in which the hydrogen of the paraffin is replaced by the hydroxyl group, OH. They are called *alcohols* after their best known and most important member.

If a hydrogen atom in methane, CH<sub>4</sub>, is replaced by hydroxyl, the formula becomes CH<sub>3</sub>OH and the corresponding substance is called *methyl alcohol*. Its commercial name is wood alcohol. In the same way C<sub>2</sub>H<sub>5</sub>OH is derived from ethane and is called *ethyl alcohol*. This is the ordinary alcohol or "spirits."

Alcohol is made by allowing sugar solutions, *e.g.*, fruit juices, to ferment. The fermentation depends upon the life of a fungus called yeast; it is composed of cells arranged like a string of beads, each of which increases by sending out shoots to develop into new cells. The latter finally separate, but for a time the tiny cells stay in parallel rows. The cells take energy for their growth from the decomposition of the sugar, which under the influence of a catalyzer, or *ferment*, called *zymase*, decomposes, with loss of energy, into alcohol and carbon dioxide. The sugar concerned in this reaction (there are numerous other sugars) has the composition C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>, and the general equation is



Carbon dioxide, therefore, is formed in addition to the ethyl alcohol, and causes the foaming of all fermented liquors.

The phenomenon can readily be studied by diluting honey with water and adding yeast to the liquid. Honey is essentially a concentrated solution of a sugar that is readily fermented. Yeast is composed of fungus which is capable of reproducing itself, and the cells begin to increase at once when placed in a sugar solu-



tion; thus in an hour or so, depending on the temperature, the generation of gas and the formation of alcohol is evident. If the liquid is distilled after a few days, an aqueous distillate is obtained in which alcohol can be recognized by its well-known taste and smell.

This process is carried out on an extensive scale, and not only fruit juices but also other plants containing starch instead of sugar, as potatoes or grain, are made to ferment. By a reaction to be explained later the starch is changed to sugar and the sugar is then allowed to ferment. Alcohol is separated from the fermented mass by distillation. Wine, beer, and other alcoholic drinks are made in a similar way. Rum, brandy, whisky, etc., are made by distillation, while wine and beer are not distilled and therefore contain the fermentation residues.

Ethyl alcohol or "spirits of wine" is a colorless liquid which boils at  $78^{\circ}$  and is inflammable. It dissolves in water in all proportions, producing a marked contraction in volume which may be plotted as described on page 204. Comparatively few salts are soluble in alcohol, but many substances of organic origin, besides bromine and iodine, do dissolve in it. Although the use of alcohol for drinking purposes has fortunately begun to decrease, as its great harmfulness becomes more and more generally recognized, its technical and industrial application is rapidly increasing. It is used in the household as fuel for small lamps and stoves, and for this purpose is often "denatured," or treated with some foul-smelling organic substance, to make it unfit to drink. In chemical factories it finds extended use as a solvent and also as a source of countless other derivatives.

**230. Ether.** — Dehydrating agents change alcohol to ether, which may be considered as the anhydride of alcohol. Ether has the composition  $(C_2H_5)_2O$  and is formed according to the equation  $2 C_2H_5OH = (C_2H_5)_2O + H_2O$ . It is a very light, volatile liquid, boiling at  $33^{\circ}$ ; it is exceedingly inflammable and has a characteristic sweet odor. Ether acts as an anesthetic and is used to produce unconsciousness during surgical operations. It has numerous uses in chemical industries.

If ether and water are shaken together they do not mix com-

pletely. On the contrary water dissolves only about one-tenth of its volume of ether and ether about one-thirty-third of its volume of water. The two liquid solutions are then saturated. If, then, the two liquids are mixed in any proportions, the two saturated solutions are always formed — ether with 3 per cent water and water with 10 per cent ether. The relative amounts of the two solutions depend on the proportions of the original mixture. The composition of each solution is unchangeable, however, if the mixture contains more than 3 per cent of water and more than 10 per cent of ether.

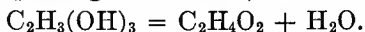
The behavior described here for ether and water holds for all pairs of liquids which are not mutually soluble in all proportions, as are water and alcohol, or water and sulphuric acid. The solubility of one liquid in another is frequently very small but is never absolutely zero. For instance, petroleum is said to be insoluble in water. If, however, water is shaken with a few drops of petroleum and the aqueous part freed from the oil as completely as possible, either by filtration or settling, the water still smells and tastes of petroleum, showing that some has dissolved. Petroleum also dissolves a trace of water, as can be shown by suitable means. The concentration at which saturation occurs may be exceedingly small but will always have a finite value.

**231. Other alcohols.** — The methyl alcohol mentioned above is the first member in the series of homologous alcohols derived from the homologous hydrocarbons (p. 278) by replacing one hydrogen by hydroxyl. It, too, is a colorless, inflammable liquid soluble in water in all proportions. It is very similar to ordinary alcohol and is called "wood alcohol" because methyl alcohol is one of the constituents of the complex mixture formed by the dry distillation of wood. Wood alcohol has about the same industrial uses as ethyl alcohol.

The alcohol derived from pentane is called *amyl alcohol* and is one of the impurities of common alcohol, as it is formed to a slight extent by fermentation. It has a bad odor and is often called "fusel oil."

**232. Acetic acid.** — If common alcohol is oxidized, it takes up another atom of oxygen, loses water, and forms *acetic acid*.

The reaction may be considered to consist of the substitution of three hydroxyl groups for three of the hydrogen atoms in ethane, followed by the splitting off of water,



This oxidation also takes place under the influence of a tiny living organism, the vinegar plant, or "mother of vinegar." The germs of this fungus, as well as those of the yeast fungus, are widely scattered, so that the ferment develops rapidly and readily wherever alcoholic liquors are exposed to the air. This is the reason for the souring of wine and beer. To carry out the process on a large scale, the acetic ferment is cultivated in large wooden vessels containing beech shavings. A dilute solution of alcohol is allowed to trickle down over the shavings and at the same time enough air is supplied to accomplish the oxidation.

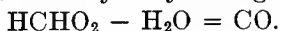
During the dry distillation of wood, not only wood alcohol but also acetic acid is formed in fairly large amounts. This crude "pyroligneous acid," containing numerous impurities, is neutralized with lime. The resulting solution of calcium acetate is evaporated to dryness and the salt heated to destroy volatile impurities. It is brought on the market in this form to be worked up into pure acetic acid.

The latter is made by distilling the salt with sulphuric acid. Acetic acid,  $\text{C}_2\text{H}_4\text{O}_2$ , or  $\text{HC}_2\text{H}_3\text{O}_2$ , passes over as a colorless liquid; it has a suffocating acid odor and is of about the density of water, in which it dissolves in all proportions. At  $16^\circ$  the anhydrous acid hardens to ice-like crystals, and for this reason it is called "glacial" acetic acid. A dilute solution of from 3 to 6 per cent acid is used as vinegar.

Acetic acid is a monobasic acid. Its salts, called acetates, are mostly soluble in water. Acetic acid is one of the weaker acids.

**233. Other acids.** — Besides acetic acid there are, of course, as many homologous acids as there are hydrocarbons and alcohols. Only the first of the series will be mentioned briefly, the acid of the composition  $\text{HCHO}_2$ . It is a liquid much like acetic acid, and is called formic acid because it was first found in ants (Latin, *formica*, an ant). It occurs also in the stings of nettles and in some other living things. Its salts may be made by pass-

ing carbon monoxide over heated bases. Sodium hydroxide gives sodium formate,  $\text{NaOH} + \text{CO} = \text{NaCHO}_2$ . This is a reversal of the experiment described for preparing carbon monoxide in which the latter was made by dehydrating formic acid,



The higher homologues of formic and acetic acids, *i.e.*, those containing more carbon, are the *fatty acids*, *i.e.*, the acids present in the natural fats. Soaps are their alkali salts; if these are dissolved in water and any strong acid added, the fatty acids separate as white insoluble precipitates, which melt easily to oily liquids.

**234. Carbohydrates.** — Closely related to the alcohols, but much more complex in composition, are some very important vegetable substances, one of which, *starch*, has already been mentioned. They are called carbohydrates because they contain, besides carbon, the elements oxygen and hydrogen in the proportions to form water, *i.e.*, twice as many atoms of hydrogen as of oxygen.

Starch has the composition  $(\text{C}_6\text{H}_{10}\text{O}_5)_x$  and was the first recognized product of the decomposition of carbonic acid in green plants (p. 257). If a plant is kept a few days in the dark, the starch originally present in the green parts will be used up. If now the plant is put back in the sunlight and half of a leaf covered with black paper so that only a part is exposed to the sun's rays, a microscopic section shows starch grains (colored blue by iodine, p. 175) present in the exposed part, while the covered half shows no starch grains at all.

The plants transport the starch from the leaves to the places where it will be needed later. It is especially needed in the seeds, bulbs, etc., from which the new plants will develop subsequently. The young plant, during the first period before it has formed any green parts, is not able to use the carbon dioxide of the air for its nourishment, and so during this period it must have a supply of starch for its subsistence. These starchy parts furnish food for men and animals.

Starch is a white powder, insoluble in water, and, as may be seen under the microscope, is composed of very thin layers. It is

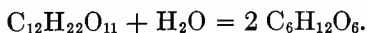
changed by hot water into a semi-liquid mass, *starch paste*, but is not really dissolved. The paste is used for laundry purposes, sizing, finishing calicos, etc.

If grain, such as barley for example, is made to sprout by moistening it with water and letting it stand in a warm place, the young plants generate a substance which, by its catalytic action, can change the insoluble starch into soluble compounds, so that the tiny plants are able to transport the food to the places where it is needed. If this sprouted grain (malt) is ground up with warm water and the mash allowed to stand for a time, it changes to a thin liquid with a sweet taste, due to its content of sugar. This can easily be fermented by yeast (p. 280).

The catalytic substance which changes starch into sugar is called *diastase*. The growing plants form so much of it that not only the starch in their own grains but also large amounts of starch from other sources can be converted into sugar. Malt, therefore, is used to change the starch in potatoes and other vegetables to sugar, so that alcohol may be made from them. Since sugar differs from starch in composition only by the elements of water, the process may be represented by the simple equation  $C_6H_{10}O_5 + H_2O = C_6H_{12}O_6$ . The reaction with water alone does not go with measurable velocity, but goes rapidly under the influence of diastase.

**235. Sugar.** — Sugar of the formula  $C_6H_{12}O_6$ , as it results from the above chemical reaction, is different from the ordinary sugar of the household, which has the composition  $C_{12}H_{22}O_{11}$ . The latter is obtained from the sugar cane or from the sugar beet, in the cells of which it is present. The juice is pressed out or removed by treatment with water, whereby the sugar leaves the cells without bringing with it many foreign substances. The purified solution is brought to crystallization. As simple as the process appears from a chemical standpoint, it requires for its technical application the use of complicated machinery to reduce, as far as possible, the cost of production and the factory losses.

Cane sugar,  $C_{12}H_{22}O_{11}$ , on taking up a molecule of water breaks down into two molecules of fermentable sugar,



In this process two different sugars are formed, both having the same empirical composition. Similar cases are of frequent occurrence in the chemistry of the carbon compounds, and substances of the same empirical composition but of different properties are called *isomers*. We have met with the same thing before in connection with sulphur and phosphorus, but in these cases the phenomenon was called polymorphism because of differences in crystal form.

The two kinds of sugar,  $C_6H_{12}O_6$ , made from cane sugar are called *grape sugar* and *fruit sugar*, or *dextrose* and *levulose*. The transformation occurs with water alone, though extremely slowly. It can be hastened by allowing a strong acid like hydrochloric to act on a sugar solution. Yeast also contains a substance called *invertin* which is capable of catalyzing the reaction. This is the reason that although cane sugar does not ferment as quickly with yeast as does grape sugar or fruit sugar, both of which ferment directly, the fermentation begins after enough of the other sugars has been formed by the invertin.

### § 31. THE LAW OF GAS VOLUMES.

**236. Simple volume relations.** — It has already been mentioned that when two or more gases take part in a chemical reaction their reacting volumes (under the same conditions) stand in the relation of simple whole numbers. Oxygen and hydrogen unite to form water in the relative quantities by volume of 1 : 2, and the water formed, if in the gaseous state and under the same conditions of temperature and pressure, has the volume occupied by the hydrogen before the combination. Chlorine and hydrogen unite in equal volumes, and the volume of the resulting hydrogen chloride is the sum of the volumes of the two gases; we have, in this case, the volume relations 1 : 1 : 2. If sulphur burns to sulphur dioxide or carbon to carbon dioxide, the volume of gas does not change, because the resulting compound occupies the same space as the oxygen did, and the volume relation is 1 : 1 in each case.

If it is asked whether these regularities are the expression of a general law, it must be determined whether or not the relation-

ships hold under varying conditions. Only if they do hold can it be considered a general law.

Physics teaches that all gases, regardless of their chemical differences, behave exactly the same toward changes in pressure and temperature. If, then, two gas volumes are equal at a given temperature and pressure they are also equal at all other temperatures and pressures, provided the two gases are always compared under the same conditions. Since the law of simple volumes holds at one temperature and pressure, it must hold at all other temperatures and pressures and is, therefore, a general law of Nature.

If now we imagine all substances that can be transformed into the gaseous condition (and theoretically we assume that all material can be changed into gas at low enough pressure or high enough temperature) existing as gases side by side under like conditions and in quantities proportional to their combining weights, then the volumes of these gases would be equal or in the relation of simple whole numbers. If we consider the smallest of these volumes as the unit, we can say that all compounds of substances with each other are formed from whole units and that the resulting compounds are also whole units or multiples. Quantities of material other than those determined by this unit are never required.

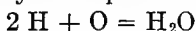
**237. Relation to the atomic theory.** — It is evident that these relationships are very much like those assumed in the atomic theory. Just as substances combine only in the ratio of whole atoms, so also they combine only in proportion to whole volume units. The conclusion can be drawn that equal volumes of different gases contain the same number of atoms. In this definition, however, the smallest groups of the compound substance formed from elementary atoms are also called atoms because a separation into single atoms would mean the destruction of the compound.

At first sight these assumptions seem to agree well. Oxygen is 16 times as dense as hydrogen and has 16 times as great an atomic weight. The same is true of chlorine, nitrogen, etc.

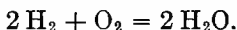
If the compounds are considered, however, contradictions

appear. The atomic weight of water,  $\text{H}_2\text{O}$ , is 18; its vapor should then be 18 times as dense as hydrogen instead of being only 9 times as dense, as is actually the case. Similar discrepancies are shown in other ways. One volume of oxygen and two of hydrogen unite to form one volume of water vapor rather than two. Since each single oxygen atom could make only one water atom, only *one* volume of water vapor ought to result from one volume of oxygen. Since two volumes are formed, an atom of water vapor would have to be composed of one atom of hydrogen and *one half* atom of oxygen. Since the assumption of half atoms is not justified, this is again a contradiction.

**238. Molecules.** — It is therefore impossible to retain the assumption that equal volumes of gases contain equal numbers of atoms, if we do not admit the existence of half atoms. Another assumption then must be made, namely, that elementary gases do not consist of simple atoms. If, for example, we assume that hydrogen gas, nitrogen gas, oxygen gas, etc., are formed of double atoms, then their chemical symbols in the gaseous state may be written  $\text{O}_2$ ,  $\text{H}_2$ ,  $\text{N}_2$ , while in the compounds the original symbols are retained. The actual relationships can then be reconciled with the atomic conceptions. The formation of water would be expressed *not* by the equation



but by the equation

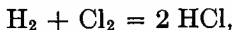


To distinguish these double atoms from simple ones they are called *molecules*. Then from two molecules of hydrogen and one molecule of oxygen, two molecules of water are formed. The volume relations are the same. We thus conclude that equal volumes of different gases do not contain the same number of atoms but the same number of *molecules*. If we assume, further, that the molecules of the above-mentioned gaseous elements are composed of two atoms, the true relations for these gases can be derived at once. It has been found that by making similar assumptions with the other elements, all the chemical reactions of gases may be represented without meeting contradictions. The *molecular theory* in this form has been generally



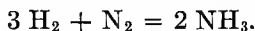
adopted in chemistry and has been found especially useful in organic chemistry.

For example, we have for hydrogen chloride the molecular equation



from which it can be seen at once that one volume of chlorine gas unites with one volume of hydrogen to form *two* (and not one) volumes of hydrogen chloride.

Another example: What is the volume relation between ammonia and the nitrogen contained in it? The molecular equation for the formation of ammonia from the elements is



Nitrogen and ammonia, therefore, are in the ratio 1 : 2, and from a given volume of ammonia half as much nitrogen must be formed. This is the actual result of the experiment on page 245.

The volume relations of the gases that take part in a chemical reaction can be computed in this way if the molecular formulas are known. It should be noted that with most elements the molecule is a double atom, while with the compounds the molecular formula is usually the simplest empirical formula, except in the case of organic compounds, so that we usually have all the information necessary for the calculation. Single exceptions will be mentioned later.

**239. Gas densities.** — The density of a substance was defined (p. 13) as the ratio of its weight to its volume; the weights of equal volumes, therefore, would have the same relations as their densities. Since, in gases, equal volumes contain the same number of molecules, the densities bear the same relations as the molecular weights, and the determination of the density of a gas gives a direct method of determining molecular weights independent of chemical analysis. The determination of gas density, therefore, is an important aid in chemical investigation. For a long time scientists have been accustomed to express gas densities in a different way than that in which the densities of liquids and solids are expressed. Whereas, in the last case, the density is equal to the weight in grams divided by the volume in cubic centimeters, this "absolute" density is used for gases only

for those special purposes in which their absolute weight is involved. Ordinarily the *relative density* is given. Since two equal gas volumes remain equal if conditions of temperature and pressure are kept the same for each gas, it is simpler to compare the weight of the gas with the weight of the same volume of a standard gas, because this relation is independent of pressure and temperature, although the absolute density changes materially with both of these factors. Air formerly served as this standard gas, and values of relative gas density were obtained bearing a definite relation to the molecular weights and from which the latter could be calculated. It is obviously simpler, however, to choose such a gas as standard that the relative densities will be the same as the molecular weights. Since the molecular weight of oxygen is 32 ( $O_2 = 2 \times 16$ ), this gas would have to be 32 times less dense. Such a gas is not known, but this is immaterial, as it is used only for purposes of computation and its properties are sufficiently defined when we say that its molecular weight is *one* and that it follows the gas laws for pressure and temperature changes.

The weight of 1 cc. of oxygen under standard conditions, *i.e.*, 76 cm. barometric pressure and at  $0^\circ$  C., is 0.001,429 g.; that of the normal gas is  $\frac{1}{32}$  as much, or 0.000,044,68. At any other pressure,  $p$ , it is larger in the ratio  $\frac{p}{76}$ , if  $p$  is measured in centimeters of mercury. At another temperature,  $t^\circ$  C., it is lighter than at  $0^\circ$  in the ratio 273:  $(273 + t)$ . At a pressure  $p$  and at a temperature  $t^\circ$ , 1 cc. of the normal gas weighs  $0.000,044,68 \frac{p}{76} \cdot \frac{273}{273 + t}$  and  $v$  cc. weigh  $v$  times as much. If, then, we have determined that a certain gas or vapor at  $t^\circ$  and under pressure  $p$  has the volume  $v$  and weighs  $w$  g., its relative density or molecular weight,  $M$ , is equal to  $w$  divided by the weight of the normal gas, or

$$M = \frac{w \times 76 \times (273 + t)}{0.000,044,68 \times 273 \times pv} = 6,230 \frac{w (273 + t)}{pv}.$$

The values  $w$ ,  $p$ ,  $v$ , and  $t$  must be determined, therefore, for the given gas or vapor, whereupon, by substituting them in the

equation, the relative density or molecular weight,  $M$ , is determined. Take, for example, a thick-walled liter flask and provide it with a rubber stopper and glass stopcock (Fig. 71). Evacuate the flask with a suction pump and weigh it. Now connect the stopcock with an apparatus furnishing dry carbon dioxide and allow this gas to fill the flask under atmospheric pressure; determine the room temperature,  $t$ , and the barometric pressure,  $p$ , and again weigh the flask. Its gain in weight is  $w$ , corresponding to the weight of carbon dioxide present, and in this case the volume  $v$  is one liter, = 1000 cc. Substitute these four values in the above equation for  $M$ , and in this way a number approximately 44 should be obtained, because the molecular weight of carbon dioxide is 44.

There are many different kinds of apparatus used to determine gas density and in this way molecular weights. They differ according to the object, the temperature at which they are to be used, the accuracy desired, etc., but it is necessary in all cases to measure the four determining factors, *weight*, *volume*, *pressure*, and *temperature*.



Fig. 71.

**240. Vapor density determinations.**— The determination of the vapor density of substances is of great importance in organic chemistry, as it makes possible valuable conclusions concerning the mutual relations of substances. There are, for example, a great many hydrocarbons containing twice as many atoms of hydrogen as of carbon, represented therefore by one of the formulas  $\text{CH}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_3\text{H}_6$ ,  $\text{C}_4\text{H}_8$ , etc., but chemical analysis cannot show which is correct. A measurement of vapor density, however, gives the desired value at once; for instance, if  $M$  is found to be 56, it is evident that the compound is  $\text{C}_4\text{H}_8$  and no other, because  $4\text{C} = 48$  and  $8\text{H} = 8$ , making a total of 56.

Of the many forms of apparatus constructed for measurements of this kind, that devised by Victor Meyer is one of the simplest. It consists (Fig. 72) of a long-necked, flask-shaped vessel that can be heated by a vapor mantle to a suitable tem-

perature (at least 10 to 20 degrees above the boiling point of the substance). By means of the simple arrangement shown on a large scale in Fig. 72, a tiny glass bulb, in which a weighed amount of the liquid is sealed, can be dropped into the heated vessel without opening the apparatus. First of all, the apparatus filled with air is heated until its temperature is constant; the outlet tube is then connected by rubber tubing with a gas-measuring tube which is calibrated in cubic centimeters and is attached to a water-leveling bulb. At the beginning of the experiment the water in the measuring tube should be at zero and the water in the balance bulb at the same level, after which the little bulb of substance is allowed to fall into the heated space,

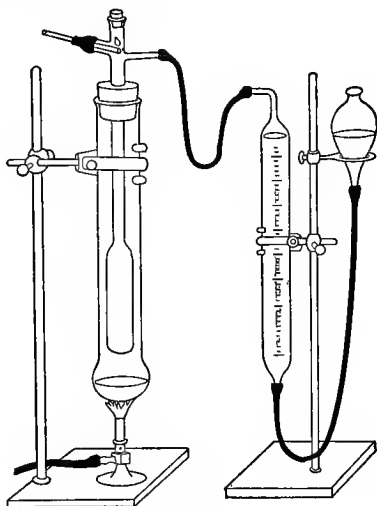


Fig. 72.

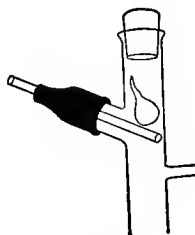


Fig. 73.

where it breaks, or is burst by the expansion of the liquid in it. The vapor at once displaces an equal amount of air, driving it over into the measuring tube. Here it cools down to room temperature, and, after a few moments, a lowering of the movable bulb, until the water in it is level with that in the measuring tube, shows by its constant level that no further generation of

gas is taking place. The volume of air is then read, the height of the barometer measured, and the room temperature taken. The weight of the vapor is known, for it is equal to the weight of liquid in the little bulb, so that the four factors needed to calculate the molecular weight,  $M$ , have been determined. This arrangement has the advantage that a measurement of the temperature of the vapor is not necessary. The vapor drives out of the apparatus a volume of air equal to its own volume, and at the same temperature. When this volume of air passes into the measuring tube it cools down and its volume becomes less. In fact, its volume has been reduced to exactly the same volume that the vapor would have occupied at room temperature if it could have been cooled down without liquefying; for the volumes of all gases and vapors change proportionately with change in temperature. This is the reason that the temperature of the cooled air and not that of the hot vapor is substituted in the formula. The vapor actually occupies a greater space in the hot apparatus than the cooled air does, but an exactly equal space was occupied by the air when it was within the apparatus before the vapor displaced it. Only in case the volume of *heated vapor* or *heated air* had been measured would it have been necessary to substitute in the equation the temperature of the apparatus. Since the volume of *cooled air* was measured, its temperature is all that is needed.

The experiment may be made most easily with ether (p. 281), in which case water may be used to furnish vapor for the heating mantle. Under these conditions 1 g. of ether will occupy about 400 cc., so that an amount of ether suited to the capacity of the instrument should be weighed out. The correct value for ether is 74.1; it will usually be found somewhat smaller.

CHAPTER X.  
THE EARTH'S CRUST.

§ 32. ALUMINIUM.

**241. Metallic aluminium.** — Aluminium is a light metal, the compounds of which are very abundant in Nature. Although the element in the free, metallic condition was formerly a chemical curiosity, it is now made from the oxide in large quantities by means of the electric current, and is used in making all sorts of everyday articles. Its general properties have become universally known in this way.

Aluminium is a silver-white metal of about the same strength and toughness as zinc. Its most striking property is its low density, and since it is now often used to make articles which had previously been made from the heavy metals, the lightness of aluminium objects is noticeable. It is, however, much denser than potassium and sodium, for its density is 2.7, or about that of glass. It melts at  $660^{\circ}$ , can be rolled and pressed well, but clogs a file badly. It is apparently unchanged in the air even when heated; it is not attacked by pure water, so that it can be used for making kitchen utensils. It can be beaten out to exceedingly thin sheets, like silver or gold, and can be crushed to a fine powder, aluminium bronze powder. It will burn when in the finely divided condition; if a thin piece of aluminium foil is held in the flame it glows and changes to oxide. Aluminium powder can be lighted by blowing it into a flame, but it does not burn as easily as magnesium.

These phenomena would make it seem as if aluminium had a very slight affinity for oxygen at ordinary temperatures. This is contradicted by the following experiment. Place a few drops of mercury on an aluminium plate; the latter is not wet by the liquid. Now add a few drops of hydrochloric acid and rub the

plate vigorously with a bit of paper or cloth; the aluminium soon becomes plated and a fairly large surface, showing the silvery luster of metallic mercury, can be obtained. This lasts only a few seconds, however; by watching closely it is seen that a white mossy growth is developing on the mirror surface, particularly if it is slightly moistened by the breath. At the same time the plate gets warm, as can be felt with the back of the hand. After a while these phenomena stop, and, if the surface coating is removed, the aluminium will be found to be strongly attacked, although free from the mercury, which will be found in the form of small gray drops mixed with the white mass that has been formed.

The experiment is not difficult to explain. Aluminium is really a metal having a great affinity for oxygen, with which it reacts energetically even at ordinary temperatures. As soon as it comes into the air, however, it becomes coated over with a thin layer of its hydroxide, which sticks like varnish and completely protects the metal beneath. This coating is not visible, as it is colorless and is so thin that it is perfectly transparent. If this coat is removed by rubbing or filing, a new one forms at once, so that the protective covering repairs itself whenever it is injured and in this way effectively protects the metal.

If now the surface is plated with mercury, or "amalgamated," the particles of hydroxide cannot stick together, as they lie upon a liquid. The coating already formed protects the metal at first even against the action of mercury, but the layer can be removed by hydrochloric acid; the mercury then amalgamates the aluminium by dissolving a part of it, and the unprotected part is oxidized at once by the oxygen of the air. The reaction goes on until the mercury is removed from the surface by the oxide formed. The reaction, then, is not characteristic of aluminium-mercury, or aluminium-amalgam, but is due to the behavior of the aluminium itself, unhindered by the protection which is usually furnished by the coating on its surface. Aluminium articles have to be carefully protected from mercury for the above reason, as amalgamation by direct contact is possible.

**242. Aluminium hydroxide and aluminium oxide.** — The aluminium hydroxide, formed as described above, has the composition  $\text{Al}(\text{OH})_3$ , and shows by its formula that aluminium belongs to a new class of metallic elements because it is *trivalent*. The oxidation process in moist air is represented by the equation



The same compound is formed whenever any aluminium salt is precipitated by sodium hydroxide as described in speaking of magnesium hydroxide (p. 192). Aluminium hydroxide is insoluble in water, and on precipitation appears as a white mass resembling starch paste. It is very difficult to wash the mass free from salts, and it does not show an alkaline reaction to litmus. Common clay, the well-known substance used in making bricks, tiles, retorts, etc., is a salt of aluminium. The name "aluminium" itself comes from the word *alumen*, alum, because this salt also contains the element aluminium.

Aluminium hydroxide occurs in Nature as bauxite.

The anhydride of aluminium hydroxide is *aluminium oxide*, which has the composition  $\text{Al}_2\text{O}_3$ . Since aluminium is trivalent and oxygen bivalent, one combining weight of aluminium cannot be saturated with oxygen. It is necessary, therefore, to take two combining weights of aluminium, the six valences of which can be satisfied by three combining weights of oxygen. The formula also expresses this relation if the bonds are indicated (p. 192).

The aluminium oxide made by heating the hydroxide is amorphous. It occurs in Nature, however, in the crystalline condition. The coarsely crystalline mineral is called *corundum*. Pure and beautifully colored forms of the oxide are called *ruby* when red and *sapphire* when blue; the color is due to small amounts of the heavy metal oxides. Because of their hardness and brilliancy, the ruby and the sapphire are valuable precious stones. Recently aluminium oxide has been melted at a very high temperature and made to crystallize, so that artificial rubies and sapphires can be made at moderate cost. These equal the natural gems in beauty and all their other properties.

A form of corundum which is somewhat less coarsely crystalline and is usually colored dark brown by iron oxide is called *emery*

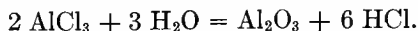


and is an important technical material. The crystallized oxide is very hard, next to the diamond the hardest of all natural substances. Emery, therefore, is used as an abrasive for polishing hard objects. Emery paper or emery cloth is made by gluing particles of suitable size to paper or linen, and emery wheels are prepared by cementing the particles in the shape of disks or rolls which can be rapidly rotated. If the hardest steel is held against an emery wheel, fine particles of metal are torn off and become so hot from the friction that they ignite. This is the reason for the shower of sparks from the point where the steel strikes the emery, and the metal is soon worn down, no matter what its hardness may be.

**243. Thermite.** — The great affinity of aluminium for oxygen is taken advantage of in the use of aluminium powder to “reduce” other oxides, *i.e.*, to change them to the corresponding metals. If, for example, three parts by weight of ignited iron oxide are mixed with one part of aluminium powder and the mixture shaken into a crucible, the mass can be ignited by a fuse of burning magnesium. The aluminium burns with the evolution of much heat; it changes to aluminium oxide and molten metallic iron is formed, which because of its greater density sinks to the bottom of the crucible. The reaction is used not only to set free metals from their oxides but also to produce a very high temperature at a given point. The aluminium acts as a carrier of a large amount of energy in a small space. This is, of course, the energy which is furnished by the electric current in the production of the metal and is stored up in it. The mixture of aluminium and the oxide of another metal is called *thermite*.

**244. Aluminium chloride.** — Aluminium dissolves in hydrochloric acid with liberation of heat and evolution of hydrogen, forming aluminium chloride, which, because of the trivalence of aluminium, has the formula  $AlCl_3$ . Anhydrous aluminium chloride is made by heating aluminium in a stream of chlorine or gaseous hydrogen chloride; in the first case direct union occurs, while in the second hydrogen is liberated. Aluminium chloride formed in this way is a white, readily volatile crystalline mass which dissolves in water with the liberation of much heat.

The anhydrous salt cannot be made from its aqueous solutions. On evaporation, a salt containing 2 H<sub>2</sub>O as water of crystallization is obtained, and any attempt to dehydrate it causes a loss of hydrogen chloride, leaving aluminium oxide,



This is the reverse of the usual reaction in which oxide and acid disappear to form a salt and water; in this case the salt and water disappear, forming the oxide and acid. If corundum or any *crystalline* form of aluminium oxide is treated with hydrochloric acid, there is no reaction, but *precipitated* aluminium hydroxide dissolves in hydrochloric acid, forming aluminium chloride, which on evaporation and heating behaves as just described.

These facts show that aluminium hydroxide is not a strong base, for sodium and potassium chlorides do not behave like aluminium chloride and are not decomposed by water vapor even at a high temperature. On the other hand, the tendency of this reverse reaction to take place can be noticed with the chlorides of the bivalent metals, calcium and magnesium. When crystallized calcium chloride is heated, it loses an appreciable, though small, amount of hydrogen chloride and the melted salt reacts weakly alkaline. Magnesium chloride, on the other hand, loses much more hydrochloric acid when similarly treated and can be almost completely transformed into the oxide by long heating with water vapor. This reaction has in fact been tried as a technical method for making hydrochloric acid.

The slight basicity of aluminium hydroxide is shown in other ways. An aqueous solution of aluminium chloride does not react neutral, like all the chlorides previously described, but is distinctly acid. This is because the decomposition of the salt by water with the formation of an acid and a base takes place in the aqueous solution, though to such a slight extent that the aluminium hydroxide is not precipitated. Such a decomposition of a salt into an acid and a base by the action of water is called *hydrolysis*; thus we say that aluminium chloride is partly hydrolyzed in aqueous solution. All other aluminium salts behave similarly.

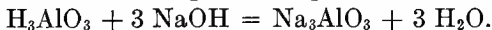
Hydrolysis takes place when either the acid or the base of a salt is weak, and is most pronounced when both the acid and the base are weak.

**245. Aluminates.** — If sodium hydroxide (or potassium hydroxide) is added to an aqueous solution of aluminium chloride, the resulting aluminium hydroxide separates at first in the form of a gelatinous precipitate as described above. If now more of the caustic alkali is added, the precipitate redissolves, giving a clear liquid with alkaline reaction.

Metallic aluminium on being treated with sodium hydroxide solution generates hydrogen and dissolves exactly as it does in acid. If hydrochloric acid is added cautiously to the solution, a precipitate of aluminium hydroxide is formed.

Aluminium hydroxide, therefore, is a substance which can unite with a base and be separated from the compound by an acid. If a solution of aluminium hydroxide in sodium hydroxide is evaporated, a very soluble, indistinctly crystalline mass is left.

The explanation of these phenomena is that the hydrogen of aluminium hydroxide really behaves like the hydrogen of a very weak acid. It does not show an acid reaction toward litmus, to be sure, because it is not soluble, but it does have the power of forming salts with strong bases. Aluminium hydroxide, then, is a base and an acid at the same time, though both of these properties are very weak. The acid properties of aluminium hydroxide are expressed by the formula  $\text{H}_3\text{AlO}_3$ , in which it appears as a tribasic acid like phosphoric acid (p. 302). It reacts with caustic soda according to the equation



The resulting salt is called *sodium aluminate*, and salts of the same general type are all known as aluminates.

**246. Alum.** — It has already been mentioned that the name aluminium comes from alum. Alum is a salt which has been known for a long time and is characterized by its beautiful octahedral crystals. It has the formula of a double sulphate of aluminium and potassium,  $\text{Al}_2(\text{SO}_4)_3 + \text{K}_2\text{SO}_4 + 24 \text{H}_2\text{O}$  or more simply  $\text{AlK}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$ . It can be formed by the oxidation of alum shale (a clay containing iron, sulphur, aluminium,

and potassium), and for a long time was the only aluminium salt of technical importance. The reason for this was that other aluminium compounds crystallize badly and could not be obtained as easily in the pure state. Aluminium sulphate is now much used instead of alum, for the potassium sulphate is not essential.

If concentrated solutions of  $\text{Al}_2(\text{SO}_4)_3$  and  $\text{K}_2\text{SO}_4$  are brought together and shaken, a precipitate of small octahedrons of alum usually results at once. The precipitation takes place more readily if a trace of alum crystal is added.

A large group of alums of varying composition is known. Other trivalent metals may be substituted for aluminium, other univalent elements for potassium; and the sulphates form double salts, also crystallizing in octahedrons, as in the case of the common potassium aluminium alum. We are dealing here with a group of isomorphous substances.

### § 33. PHOSPHORUS.

**247. Phosphorus.** — Phosphorus was discovered by the alchemist Brandt in an attempt to make gold by distilling the residue left after the evaporation of urine. He obtained a wax-like substance having the remarkable property of being luminous in the air without really burning. Brandt did not tell his secret and tried to sell his product at a high price, but the process was soon discovered by Kunkel in Germany and by Boyle in England. It was found later that bones are a much more productive source of phosphorus. It gets its name from its luminosity.

Phosphorus is a colorless substance,<sup>1</sup> which crystallizes in the isometric system and melts at  $44^\circ$ . It glows in the air, as stated, and we now know that this is due to a slow combustion. Very slight warming in the air causes quick combustion, and on this fact depends the use of phosphorus on matches; the heat of friction is enough to light the phosphorus in the head. Phosphorus boils at  $287^\circ$ , but at the same time a remarkable change takes place and can readily be observed. If a small piece of phosphorus is placed in a test tube, which is loosely stoppered to

<sup>1</sup> Impure phosphorus is more or less yellow in color.

partly shut off the air supply, and is then heated, it soon uses up the small amount of oxygen present in the tube and can then be heated further without taking fire. Just before it begins to boil a red crust forms, and sufficient heating will transform the phosphorus completely into the red mass. The red product is prepared on a commercial scale in the same way and is really phosphorus in another form. Phosphorus is therefore dimorphous, though the two different forms are much more different than are the various forms of sulphur.

Red phosphorus comes on the market in the shape of a dark-red, indistinctly crystalline mass which, unlike the white form, is not luminous in the air. It fails, too, to show the slow oxidation or the easy ignition of the other form. Place a small piece of red phosphorus and one of the white variety on an iron plate and place a lamp underneath in such a position that the red phosphorus is much nearer the heated spot than the colorless phosphorus. In spite of the greater heat applied to the red phosphorus, the yellow form takes fire first. Red phosphorus is harmless, although the colorless form is exceedingly poisonous. The two forms behave as if they were entirely different substances.

We have seen, however, that colorless phosphorus can be changed to red phosphorus by heat. If, on the other hand, red phosphorus is heated it is volatile only at a very high temperature, but drops of yellow phosphorus are deposited from the vapors. Whereas yellow phosphorus changes to red below its boiling point, the reverse change takes place only when the red form is vaporized and the vapor quickly condensed.

The reason for the great difference lies in the fact that in the transformation of yellow phosphorus into red phosphorus a large quantity of heat is liberated. The red form has much less energy, therefore, than the colorless form and is correspondingly less active.

Because of its nonpoisonous qualities, manufacturers have substituted red phosphorus for colorless phosphorus in the manufacture of matches. The so-called Swedish matches are based on this idea, though with them the phosphorus is not on the head but on the striking surface.

**248. Phosphoric acid.**—The rapid burning of phosphorus produces phosphorus pentoxide,  $P_2O_5$ . This can be seen if combustion takes place under a large glass jar; white flakes are formed which float around like snow and finally settle. If some of the powder is collected quickly and thrown into water, a hissing sound is produced as with hot iron and water. This is an indication that so much heat is generated that the water in contact with the powder boils. Phosphorus pentoxide belongs to the class of substances having a great attraction for water and it is therefore used as an extremely efficient drying agent.

The aqueous solution of  $P_2O_5$  reacts acid, as we have seen already (p. 123), and contains phosphoric acid. There are different kinds of phosphoric acid, differing essentially in the relative amounts of water and of phosphorus pentoxide which they contain. We shall study only that form which occurs in natural products. It is the most stable form and all the others are transformed into it on standing. It is called *orthophosphoric acid* and has the composition  $H_3PO_4$ .

The three hydrogen atoms are all replaceable by metals, although not with equal readiness. The acid, therefore, is tribasic, just as sulphuric acid is dibasic. It can form three different salts in which one, two, or three hydrogen atoms are replaced by metals; for example the three sodium salts are  $Na_3PO_4$ ,  $Na_2HPO_4$ , and  $NaH_2PO_4$ . These salts are distinguished by the names tri-, di-, and mono-sodium phosphate, and salts of other metals are named in the same way.

Phosphoric acid in the pure state is an indistinctly crystalline mass, freely soluble in water, to which it imparts an agreeable acid taste. In contrast to elementary phosphorus, it is not only nonpoisonous but in the form of its salts and other compounds it is a regular constituent of all living things. It seems particularly closely related to the substances of which the brain and nerves are composed, and is found in the fruit of plants. For this reason, salts of phosphoric acid form an essential constituent of fertile soil and must be furnished to it if not already present in large enough quantities. Phosphates, then, are a necessary part

of artificial fertilizers and as such have an important place in manufacturing and commerce.

If it is attempted to titrate phosphoric acid with alkali using litmus as indicator, it is difficult to obtain a satisfactory *end point*; the change in color from red to blue does not occur sharply with one drop, but takes place gradually and with a large excess of alkali. This is because the trisodium phosphate is decomposed by water according to the reaction



This, again, is the reverse of salt formation and is another case of hydrolysis (p. 298). Before the amount of sodium hydroxide which would be necessary to form trisodium phosphate has been added, hydrolysis sets in and the solution becomes blue. Since we are dealing with a reaction which is only partially complete and depends on the concentration of the reacting substances, the reaction is not a sharp one, as it is with strong acids which are practically unaffected by hydrolysis, but is a gradual change with no definite end point.

**249. Phosphates.**—Of the many different phosphates, the disodium phosphate, or ordinary commercial sodium phosphate, should be mentioned. It forms large crystals with 12 H<sub>2</sub>O and these crystals weather easily. The salt is used in medicine and in the laboratory.

The alkali metals are the only ones of which the phosphates are all soluble. With the alkaline earths, only the acid phosphates having two available hydrogen atoms are soluble, the rest insoluble. The earths and heavy metals form insoluble phosphates.

Calcium phosphate, Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, is the most important of these insoluble salts. It is found in Nature in coarse masses as *phosphorite*, and forms the chief constituent of the bones of vertebrate animals. If these bones are heated in the air, to burn off the organic matter which they contain, there remain white masses, called bone ash or bone char, which have the form of the bones, and are composed principally of tricalcium phosphate.

Tricalcium phosphate is insoluble and thus is not suitable for use as a fertilizer, as it would be too slowly attacked and dissolved by the plants. To make it more available, it is treated with sulphuric acid and converted to monocalcium phosphate,  $\text{CaH}_4(\text{PO}_4)_2$  which is fairly soluble. The resulting mixture of gypsum and monocalcium phosphate is called *superphosphate*.

### § 34. SILICON.

**250. The element.** — Silicon, next to oxygen, is the most abundant element in the earth's crust. It occurs only in compounds, from which the free element can be obtained by the action of sodium or a similar metal on a compound of silicon with chlorine or fluorine, or by heating quartz with powdered magnesium. Elementary silicon resembles elementary carbon for it exists in an amorphous as well as in a crystalline form. The former is a greenish-brown, very fine powder, the latter a hard, gray substance with metallic luster. Neither is of technical or practical importance, so that a detailed description is not necessary.

**251. Silicon dioxide.** — By far the most important compound of silicon is the dioxide,  $\text{SiO}_2$ , which as *quartz* in its various forms is widely distributed. The purest form is as transparent as glass and is called *rock crystal*. It forms regular, six-sided columns (Fig. 13, p. 32) usually capped by a six-sided pyramid. The axis of the column is a sixfold axis of revolution, *i.e.*, the crystal comes into a coincident position at each revolution through  $60^\circ$ . Rock crystal belongs, therefore, to the hexagonal system.

Quartz is usually not wholly pure but is colored milk white, pink, violet, or gray-brown by impurities; it is then called *milk quartz*, *rose quartz*, *amethyst* or *smoky quartz*. The last named is occasionally found in very large crystals, sometimes more than a meter long. It must be assumed that these giant crystals have been formed from aqueous solutions at a low temperature, for if smoky quartz is heated it becomes colorless owing to the decomposition of the coloring matter.

Quartz in small broken pieces forms the quartz sand that is found on the seashore. Under suitable conditions these tiny



grains can be united by a cementing material and joined together in a coherent mass called *sandstone*, much used as a building material.

In addition to these crystalline forms of silicon dioxide there are the amorphous forms, of which flint is the most important. This occurs as concretions in chalk deposits, and is often found in rows or layers, indicating that the individual masses have collected around organic remains. It occurs in the form of nodules which have a marked conchoidal fracture and by skillful work can be split into various forms. In prehistoric times when the metals were unknown, knives, axes, arrowheads, and other utensils made of flint played an important part. Fracture surfaces are easily obtained of which the edges are razor sharp. When flint is struck against steel, sparks form because tiny particles of metal are torn off and are at the same time so heated by friction that they take fire in the air. If flint and steel are struck together in nitrogen or other inert gas, the tiny particles are found to be rounded off by the heat, though not burned, showing that the mechanical work has produced a very high temperature.

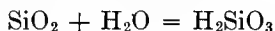
Silicon dioxide, in both its natural forms, is a hard substance, somewhat softer than the diamond but harder than most other substances. The latter are, therefore, scratched by quartz or flint. Quartz is, for this reason, of technical importance as a polishing material, and the surfaces to be cut are worked either with solid quartz or with the more or less finely powdered sand. Mirror glass, for example, is polished by moving a smaller weighted plate over a larger one after wet sand has been placed between them. The roughest places are removed by coarse sand, and as the work advances finer sand is used. The final surface is produced in other ways. Glass stoppers for flasks are ground in much the same way.

Quartz is so difficultly fusible that it is only recently that it has been successfully melted and blown like glass. At present various chemical vessels are made from "fused quartz," which is very resistant to acids and can stand sharp temperature changes without breaking. This is because the heat

expansion of fused quartz is very slight, so that no great tension can exist between the different parts of the same piece, even when they have decidedly different temperatures. For example, a quartz glass test tube can be heated red hot in a flame and plunged at once into ice water without breaking, but quartz glass can be broken by a blow as easily as common glass.

**252. Silicic acid.** — Silicon dioxide is the anhydride of an acid called silicic acid; its salts are the silicates. The greater part of the earth's crust is composed of silicates of varying composition, and the lava forced from the interior of the earth by volcanic action is also made up largely of various fused silicates.

Silicic acid has a composition represented by silicon dioxide plus the elements of water. The composition of the silicic acid salts, or silicates, shows that there is not merely one acid but several which are different because of the varying amounts of silicon dioxide and water. The two most important acids correspond to the equations of formation



and



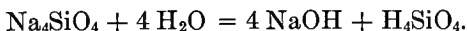
The first equation is analogous to that in which carbonic acid was formed from carbon dioxide, and the resulting acid is, like carbonic acid, dibasic. This acid is called *metasilicic acid*. The second equation gives a tetrabasic acid known as *orthosilicic acid*.

The number of silicic acids and silicates is by no means exhausted, for there are other acids in which the ratio of the silicon dioxide to water is different, for example 2 : 1, 3 : 2, etc. These more complicated relations will not be considered here.

**253. Silicates.** — The silicates of the different metals are for the most part insoluble in water; only those of sodium and potassium are soluble. The latter are made by fusing the hydroxides or carbonates with silicon dioxide (quartz sand). The vitreous mass resulting from the fusion will dissolve in water if it is finely powdered and the water boiled. Amorphous silicon dioxide is dissolved by boiling in concentrated solutions of the alkaline hydroxides.

Solutions made in this way are more or less heavy or sirupy liquids, according to the concentration. Thin layers of these solutions when exposed to air harden to a glassy sheet, so that the solutions are often called "water glass." Common glass is also made of silicates, usually a combination of sodium and calcium silicates. The presence of calcium makes the glass insoluble.

The natural silicates, which usually contain the metals potassium, sodium, magnesium, calcium, and aluminium, are all insoluble in water. Thus ordinary red feldspar, or orthoclase, is a silicate of potassium and aluminium. Mica contains magnesium and aluminium silicates; talc and soapstone are magnesium silicates. Silicates undergo in Nature a transformation, which, although it is a very slow process, is exceedingly important because of its great extent. Silicic acid is a very weak acid, as is shown by the fact that solutions of sodium and potassium silicates react alkaline to litmus. This is because water decomposes the salt, forming the hydroxide of the metals and the very weak silicic acid. It is another case of hydrolysis (p. 298). In the case of sodium orthosilicate the reaction is expressed by the equation



Hydrolysis is not complete in water-glass solutions, for part of the salt dissolves without forming sodium hydroxide and silicic acid. The more concentrated the solution, the greater the proportion of unhydrolyzed sodium silicate. Because of the separation of silicic acid from dilute solutions, water glass is kept in as concentrated solution as possible.

**254. Colloidal silicic acid.** — If a concentrated solution of water glass is treated with an acid, hydrochloric acid for example, the corresponding chloride is formed and silicic acid set free. The latter separates as a white amorphous mass, making the solution coagulate like starch paste. This experiment apparently indicates that silicic acid is insoluble in water.

If, however, the water-glass solution is first diluted, acid may be added without causing any visible precipitation. A very dilute solution will not appear to be changed, but if a solution of medium concentration (about one-eighth as strong as commer-

cial water glass) is taken and acid is added until the basic reaction has just disappeared, the liquid will at first be clear and mobile, but in a short time it becomes turbid and stiffens to a jelly-like mass, much like hard glue. After this has happened the silicic acid will no longer dissolve in water, for the silicic acid in the jelly-like mass is insoluble.

The particular condition in which the silicic acid exists here is called the *colloidal* state (the word meaning *like glue*). It represents an intermediate state between a solution and a mixture, for although the mobile liquid will run through an ordinary filter, a very fine filter will hold back the silicic acid. It is especially remarkable that the changes in condition will not take place in the reverse direction, for after the solution has once hardened it stays in the same condition even after the addition of water. Silicic acid, therefore, is really insoluble in water; but if it is separated from its salts in a dilute solution it does not pass directly into the solid form of an insoluble precipitate but stays in the colloidal condition, apparently dissolved, and the precipitation takes place very slowly, the more slowly the more dilute the solution. In concentrated solutions precipitation is at once evident.

Such a decomposition of soluble silicates can be effected not only by strong hydrochloric acid but also by weak acids. Even the exceedingly weak carbonic acid acts in the same way. The reason that water glass which has been exposed to the air for some time usually gelatinizes to a solid mass, is because carbon dioxide has acted on it, forming free silicic acid and a carbonate. The same thing takes place when a layer of water glass dries in the air. The vitreous coating that forms is composed of silicic acid. To keep the layer intact and not have it broken up by the crystallization of the carbonate, the film must be washed with water to remove the soluble carbonate, leaving behind the insoluble silicic acid. To show the decomposing action of carbonic acid, dilute an ordinary solution of water glass with about two volumes of water and pass carbon dioxide into it. At first the bubbles come to the surface and burst as they would in most other liquids, but later, when the union of carbon dioxide with

the sodium hydroxide is almost complete, a permanent foam forms, and soon after the whole mass solidifies to the well-known silicic acid jelly.

**255. Weathering of natural silicates.** — The last process is like that which takes place in Nature with the silicate rocks. The silicates are decomposed partly because of hydrolysis under the influence of water and still further by the combined action of water and carbon dioxide; part of the silicic acid separates where it is formed and the rest is carried away in the colloidal condition. The bases of the silicates are also carried away by the water, if their carbonates are soluble. Some bases form such stable salts with silicic acid that they are left behind as simple silicates. This is especially true of aluminium, the silicate of which is *clay* in its various forms. Clay is always left behind when complex silicates containing aluminium are decomposed by water and carbon dioxide, or, in other words, by their "weathering." When feldspar weathers, for example, the potassium is carried off as the readily soluble potassium carbonate and some of the silicic acid goes with it. Aluminium silicate is not decomposed, however, because carbonic acid cannot form a stable aluminium salt, and thus this silicate is left behind as a decomposition or "weathering" product. In the pure condition it is a white plastic mass called *china clay*, or *kaolin*, which is a hydrated aluminium silicate.

Another silicate often left behind by weathering is magnesium silicate, called *talc*, *soapstone*, *serpentine*, or *meerschaum*, depending on its properties. It has a curious greasy feeling and is very heat-resistant, so that it can be used for pipe bowls, gas tips, etc. It can be turned, filed, and carved, properties which make it possible to use the silicate for various ornamental and practical purposes. Green serpentine is colored by its iron content.

**256. Glass.** — The technical importance of glass, porcelain, and clay in their manifold uses is due to their properties as silicates.

Glass is an amorphous melt of potassium or sodium silicate with calcium silicate. Occasionally other silicates are added, particularly lead silicate, which makes a strongly refractive glass,

*flint glass.* Ordinary window glass is a sodium-calcium silicate; it is colorless in the pure condition, but can be colored by dissolving in it certain oxides of the heavy metals. The translucent green of common bottle glass is due to the small percentage of iron usually found in the raw materials.

In making glass, a finely powdered mixture of quartz, soda, and limestone ( $\text{SiO}_2$ ,  $\text{Na}_2\text{CO}_3$ , and  $\text{CaCO}_3$ ) in proper proportions is heated moderately. The silicic acid drives out the carbonic acid as carbon dioxide, forming the corresponding silicate, which sinters together to a porous, stony mass. The clinker is now heated strongly enough to melt the silicates, and the temperature is kept as high as possible for a while so that the insoluble matter can settle to the bottom of the thoroughly liquid mass and the gas bubbles can escape. After the vitreous mass has thus been purified, it is allowed to cool till it becomes plastic and can then be blown like a soap bubble. By keeping some parts hotter and more liquid than the rest, a large number of shapes can be made without difficulty. If it is desired to form a perfectly definite shape, the glass is blown into a mold. Tubes are made by first blowing a hollow sphere; an assistant then fastens an iron rod to a point opposite the mouth of the blowpipe and the sphere is drawn out to an ellipsoid, the middle section of which differs but slightly from a cylinder. The speed of pulling determines the size of the tube, and the wall thickness depends on that of the original ball. All glassware is placed in a large furnace after it is made and is allowed to cool off slowly (annealed). If this is not done, the glass is very brittle and breaks easily.

**257. Porcelain and clay.** — The preparation of earthenware vessels is based on the fact that hydrated aluminium silicate, the weathering product of many rocks, forms a plastic mass when wet, becomes somewhat more solid on drying, but goes to pieces when wet a second time. If, however, the dried objects are exposed to a higher temperature, or *burned*, they sinter together and the aluminium silicate loses water, whereby it is changed to a stony mass which is no longer disintegrated by water but, because of its porous nature, allows water to percolate through it. If this porous quality is useful, or harmless, as in the case of

flower pots or tiles, nothing is done, but when the article has to be water-tight, it is "glazed," or covered with a glassy surface.

The finest and most durable clay material, *porcelain*, is made from the purest aluminium silicate, or kaolin, which is usually a product of the weathering of feldspar. After some finely powdered feldspar has been added to the clay, the articles are molded, dried, and heated at a low temperature. A coating of powdered feldspar in the form of a thin cream is then put on, either by dipping or by pouring, and the object, inclosed in a fire-proof case, is heated to a high temperature. The feldspar, both on the surface and in the mass, melts and saturates the solid framework of aluminium silicate as if it were a varnish. After cooling, the glaze is merged into the mass, and thereby makes the article semi-transparent and durable.

The process cannot be carried out in the same way with ordinary clays, as they melt so much more easily than pure aluminium silicate because of the presence of foreign substances. A moderate burning is enough in this case, and the glazing is accomplished by making a glass of the right composition, powdering it thoroughly, putting it on in the form of a watery paste, and heating. Faïence is made if the clay is white, but if it is colored (usually from iron) ordinary earthenware results. Since lead silicate melts easily and makes a brilliant glaze, lead is often found in the glaze of cheap articles. A poisonous salt of this metal is then likely to pass into food that is prepared or kept in these dishes, so that laws have been passed forbidding the use of lead glazes.

A special sort of earthenware, called flintware, is of importance in the chemical industry and is characterized by great resistance to chemicals. The articles are made of a fire-resisting clay, burned at a very high temperature, and then glazed by throwing common salt into the furnace while the temperature is at its highest. The salt volatilizes, and under these conditions is decomposed by the water vapor present, forming on the surface of the article a double silicate of sodium and aluminium, while hydrochloric acid escapes. Since the glaze is formed from the mass itself, it is as durable as the glaze of porcelain.

A surface glaze will not usually have the same coefficient of expansion as the clay itself, so that temperature changes often cause a state of tension to exist between the glaze and the clay, finally making the weaker part, the glaze, crack. That is the reason that dishes of Faïence which have been heated are almost always covered with a network of "craze." Dirt then crowds into the spaces, leaving dark deposits, which make the cracks distinctly visible. By choosing a glaze of such a composition that its coefficient of expansion is as nearly as possible that of the mass, the difficulty can be reduced but not completely overcome.

The manufacture of enameled ironware is based on the same principle. A coarse-grained enamel is first fused on the surface to act as a carrier and on it is put a readily fusible coat which imparts the desired color and final surface.



## CHAPTER XI.

### HEAVY METALS OF THE IRON GROUP.

#### § 35. ZINC.

**258. The metal.** — In the group of heavy metals we shall first study zinc (which we have used already for making hydrogen) for it is very similar to another metal already discussed, namely magnesium. Moreover, its chemical properties are simpler than those of most other heavy metals.

Zinc in the pure state has only been known since the seventeenth century, although it is found frequently in antique objects mixed with other metals. In ancient times it was reduced from its compounds occurring in Nature with copper and lead, so that the product was a more or less complex metallic mixture or *alloy*. The reason for its late discovery was not due to its infrequent occurrence but because metallic zinc is more readily vaporized than other metals (except mercury) and in this form it burns easily. The art of distilling had to be perfected before the pure metal could be prepared, and this occupied a long period through the Middle Ages.

Zinc is a bluish-white metal, oxidizing easily in the air to a grayish-white, dull surface. In most cases, however, the oxide forms a coherent coating, practically preventing any further action of oxygen, so that the metal is fairly resistant to the action of the atmosphere. In the air of our modern large cities, in which sulphurous and sulphuric acids are present, zinc is quickly attacked because of the solubility of zinc sulphate.

Cast zinc is fairly crystalline and consequently brittle. It gets soft and tough when moderately heated, and, if rolled, will retain its toughness. The difference between a stick of cast zinc such as is used for chemical purposes and a piece of zinc foil is very marked. The former breaks as soon as an attempt to

bend it is made, while the latter can be bent through a large angle without breaking.

Zinc melts at  $420^{\circ}$  C. and boils at  $980^{\circ}$  C. The vapor burns at the high temperature as soon as it comes in contact with the air. This can be shown by placing a little zinc in a small porcelain crucible and heating over a blast lamp. The combustion takes place with a bluish-white light, but the flame is not nearly as brilliant as that which results by burning magnesium.

**259. Zinc oxide.** — The resulting zinc oxide,  $ZnO$ , forms light flakes which are found whenever zinc ores are reduced. The flaky mass was known to the chemists of the Middle Ages as "philosopher's wool" (*lana philosophorum*). It is yellow while hot and white when cold. It is used as a white pigment and is made for this purpose under the name "zinc white." It has an advantage over most other white paints in not being discolored by atmospheric gases, as almost all zinc compounds are white.

Zinc oxide does not, like magnesium, form the hydroxide directly, but the latter can be made by precipitating a zinc solution with an alkali. An excess of alkali must not be added or the zinc hydroxide will dissolve.

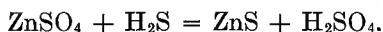
Zinc oxide is readily soluble in acids, forming zinc salts, all of which are colorless unless the acid itself is colored; the solubilities of the salts are very similar to those of the corresponding magnesium compounds. The chloride, nitrate, and sulphate are freely soluble in water, while the carbonate and hydroxide are insoluble. Zinc hydroxide is a weaker base than magnesium hydroxide. This is shown by the fact that aqueous solutions of nearly all zinc salts have a slightly acid reaction, due to a slight hydrolysis. This is characteristic of almost all salts of the heavy metals.

**260. Zinc salts.** — Zinc chloride is one of the important salts. It is an easily fusible, white mass, readily soluble in water with evolution of heat. It deliquesces in the air because the vapor pressure of the saturated solution is much less than the usual partial pressure of atmospheric moisture. The solution is readily obtained by dissolving zinc oxide or metallic zinc in hydrochloric acid; in the latter case hydrogen is generated

(p. 135). Concentrated solutions are oily in character, and when mixed with zinc oxide give a paste which quickly solidifies to a hard mass and is used by dentists in filling teeth. The zinc oxide unites with the zinc chloride and forms a basic zinc chloride, sometimes called *zinc oxychloride*.<sup>1</sup> The solution of zinc chloride is also used as a "soldering fluid," for it acts as ammonium chloride does and "cleans" a metallic surface so that molten lead and tin will stick to it. Zinc chloride is also used to protect wood, particularly railroad ties, from decomposing when in contact with damp ground.

*Zinc sulphate*,  $\text{ZnSO}_4$ , crystallizes with 7  $\text{H}_2\text{O}$  and is isomorphous with magnesium sulphate. It is called *zinc vitriol* or *white vitriol*. These old mining names are still used for all the sulphates of the heavy metals, but should be given up as unsystematic. The salt is used in medicine and in the arts, and is made by dissolving the metal in sulphuric acid, which for this purpose should be dilute. In a concentrated and hot solution of sulphuric acid the reaction goes farther, and a part of the sulphuric acid is reduced to hydrogen sulphide and sulphur.

**261. Zinc sulphide.** — Zinc sulphide is another important compound of zinc. It is obtained in a hydrated form whenever an aqueous solution of a zinc salt is treated with hydrogen sulphide or, still better, with a solution of sodium or ammonium sulphide. If hydrogen sulphide is passed into a solution of zinc sulphate, for example, the following reaction takes place:



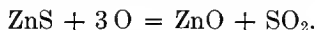
Zinc sulphide and sulphuric acid are formed. If, on the other hand, zinc sulphide is treated with an excess of sulphuric acid it is dissolved. The reaction, therefore, can take place in either direction, or is *reversible*, and the direction in which it goes depends on the relative concentrations of the reacting substances. In the above reaction only a part of the zinc (roughly  $\frac{2}{10}$ ) precipitates as sulphide; so much acid is then formed that it begins

<sup>1</sup> Such basic chlorides, which are capable of combining with more acid to form a normal or "neutral" salt, must not be confused with the salts of hypochlorous acids; *e.g.*,  $\text{NaOCl}$  is not basic salt.

to act as a solvent and prevents further precipitation. If enough sulphuric acid is added at first, there will be no precipitation.

The conditions are different if an alkaline sulphide is used; then a neutral sulphide forms and the precipitation is complete. Ammonium sulphide is commonly used in analytical work, as, owing to its volatility, it can be removed more easily if an excess has been added.

**262. Metallurgy of zinc.** — Zinc sulphide in the pure condition is a white substance used to some extent as a white pigment. It occurs abundantly in Nature and is one of the most important zinc ores. It is called zinc blende, or sphalerite. Sphalerite is commonly colored yellow, brown, or even black by impurities. The first step in making zinc is to roast the ore. This means that it is heated with a supply of air to change the oxidizable substances to oxides. The following reaction results:



The zinc changes to zinc oxide and the sulphur to sulphur dioxide. Because of its injurious action on vegetable life the latter cannot be allowed to escape into the air, so that a sulphuric acid plant is often connected with a zinc smelter and the harmful sulphur dioxide converted to sulphuric acid as a by-product. All chemical industries ought to be arranged in the same way, *i.e.*, the by-products of one reaction ought to serve, when possible, as the basis of other useful reactions.

The zinc oxide is then mixed with carbon and heated in retorts, from which the zinc distills in vapor form and is collected in suitably arranged, air-free chambers. The zinc condenses first in the form of a fine gray powder, known as *zinc dust* which has many uses in the laboratory and in the arts. After a time the flues and chambers become heated and the zinc then condenses in the liquid state.

Other zinc ores are smithsonite<sup>1</sup> and calamine. The former is zinc carbonate,  $\text{ZnCO}_3$ , and the latter a hydrated zinc silicate of varying composition. Both are reduced to obtain the zinc.

<sup>1</sup>The carbonate is often called calamine, although the name rightfully belongs to the hydrous silicate of zinc.

The carbonate is first changed to the oxide on moderate heating, but the silicate is reduced directly.

Metallic zinc is used for numerous purposes, as it is more resistant to water than iron and cheaper than copper, though the latter is much more durable. It is often used in alloys with other metals; the most important alloy is that with copper, *brass*, the well-known yellow metal used for so many purposes. Scientific apparatus of all sorts is made of brass if possible, because it can be worked easily and accurately and is sufficiently resistant to the action of air.

Zinc salts are somewhat poisonous.

### § 36. IRON.

**263. The metal.** — Iron is the most widely distributed and the most important of all the heavy metals. It is found in Nature only in combination with other elements. Meteorites form the only exception. These are small heavenly bodies that have struck the earth's atmosphere in their courses and have been so strongly attracted by the earth that they have fallen upon it. They are composed of metallic iron mixed with certain other metals, especially nickel.

The iron compounds as they occur in Nature are partly oxidic, *i.e.* containing oxides, and partly sulphidic, *i.e.* containing sulphides. The former are the only ones used directly in the production of metallic iron, and the method of smelting will be described later.

Commercial iron is not the pure metal but contains carbon in varying amounts, as well as small quantities of other elements. Pure iron is a gray, tough but not very hard metal of no practical use. Commercial iron is of three kinds, *wrought iron*, *cast iron*, and *steel*. The former is the purest and its properties are nearest to those of pure iron.

Wrought iron is tough and has the property of softening long before it melts; in this condition it can be hammered and pressed or, in technical language, "wrought." It can also be welded, *i.e.*, two pieces of iron can be joined by simply hammering. To do this the metal must be somewhat hotter than is necessary for rolling,

etc., and under these conditions the two pieces will stick together under the hammer like pieces of wax or cement. Wrought iron is not very hard and is not much changed by heat treatment. It may contain up to 0.5 per cent carbon and is otherwise fairly pure.

Steel contains not more than 2 per cent carbon and consists of a mixture of iron and iron carbide,  $\text{Fe}_3\text{C}$ . The latter is very hard and gives the steel its hardness, which can be materially changed by varying the heat treatment. Steel is hardest if it is cooled suddenly from a white heat or "quenched." This may be done by dipping it into water or some other liquid. The resulting steel is in a condition of internal strain, is so hard that it scratches glass and is thus sometimes called *glass-hard*.

If, on the other hand, the steel is heated cautiously the internal strain is reduced. The result is that the steel becomes softer and tougher. In the "glass-hard" condition it is so brittle that it cannot be bent without breaking. The hotter and longer the steel is reheated or "annealed" the softer and tougher it becomes. The amount of softening can be estimated by making a polished surface on the hard steel and then noticing the color changes on heating. The changes occur at the temperature at which the steel begins to oxidize in the air. The layer of oxide is at first thin and transparent and shows what the physicists call the "colors of thin films." The surface becomes first yellow, then brown, purple, and finally gray, after which the steel is perfectly soft again.

The phenomenon can easily be shown by quenching a glowing watch spring and then annealing it for successive periods. The quenched steel breaks when bent, and scratches glass, but becomes softer and tougher the longer it is annealed.

The steel is brought to various degrees of hardness (tempered) according to the use to which it is to be put. Balls for ball bearings are left glass-hard; iron-working tools are annealed yellow; tools for working with brass, purple, and for wood turning, blue. Watch springs are annealed to a blue or purple shade.

Steel can be worked hot. It melts at about 1400°, and can be poured (cast steel).

In addition to these ordinary carbon steels there are a great many kinds of steel to which other and often secret constituents have been added and which have different properties. Their usefulness is due to the fact that the hardness, toughness, and other properties of the metal can be modified at will to suit the purpose for which the steel is to be used.

Cast iron contains about 4 per cent carbon, and melts the most easily of the three forms. It is not tough, but offers great resistance to compression, and is used when complicated shapes are needed, as in manufacturing machinery in which the parts are to be cast. If ordinary molten cast iron is allowed to cool slowly, a part of the carbon separates, giving a dark gray, soft metal that can easily be turned, filed, and worked in other ways. If, on the other hand, the cooling takes place quickly, the carbon stays in combination with the iron, giving the metal a white appearance and great hardness. The two sorts are classified as gray cast iron and white cast iron. Gray iron is the usual form; white iron is only made when great hardness is desired, as in rolls, etc.

**264. Ferrous compounds.** — Iron forms two groups of salts; in one group it is bivalent, in the other trivalent. Compounds of the first group are similar to those of magnesium, but the compounds of trivalent iron are analogous to those of aluminium. The similarities are not only with respect to the symbols of the salts but also with respect to solubility relations and particularly with respect to isomorphism, or the fact that the corresponding compounds have the same crystalline form. For example, the oxide of trivalent iron crystallizes in the same rhombohedral form as aluminium oxide does, and the sulphate of bivalent iron forms a double salt with potassium having the same form as magnesium potassium sulphate. To distinguish the two series, the bivalent compounds are called *ferrous* and the trivalent ones *ferric* compounds.

Ferrous compounds are formed when metallic iron is dissolved in acids (other than nitric acid). Hydrogen is evolved and the

ferrous salt dissolves, imparting a pale green color to the solution. Owing to the carbon content of the metal, the hydrogen evolved on treatment with acids is contaminated with hydrocarbons. The best-known ferrous salt is the sulphate, or *iron vitriol*,  $\text{FeSO}_4 + 7 \text{H}_2\text{O}$ , which occurs in large monoclinic crystals and is often called *copperas*. If uninjured, the crystals keep for a long time, but if broken or crushed they weather easily, taking up oxygen and changing over to a ferric salt. The aqueous solution has the same color as the crystals; it has an astringent taste and oxidizes in the air, precipitating a yellow, basic iron salt. Since the iron in a ferric compound, because of its trivalence, requires one and a half times as much acid to form a normal salt as was required in the ferrous state, there is not enough acid in the ferrous salt to keep the iron in solution. Salts in which the base has not been fully neutralized are called *basic salts* (p. 315).

Ferrous sulphate is used industrially in large quantities particularly in dyehouses; it has also been used to make ink, which often contains the iron salt of an organic acid found in nutgalls, called tannic acid. Ferrous sulphate forms easily and abundantly whenever the natural sulphide (to be described later) has a chance to oxidize in the air, and the salt was known, therefore, at an early date. Before the lead chamber process (p. 237) for making sulphuric acid was devised, ferrous sulphate served as the source of sulphuric acid. It changes on heating to a basic ferric sulphate (see above), which upon further heating changes to ferric oxide and liberates sulphur trioxide. The latter is volatile, so that if the reaction is carried out in retorts, the trioxide can be collected in water, forming a solution of sulphuric acid. So little water was commonly used that a certain quantity of anhydride remained dissolved in the acid and the product fumed in the air (p. 167). Acid made in this way was called, therefore, either *fuming sulphuric acid* or, because of its production from iron vitriol, *oil of vitriol*. The name *Nordhausen acid*, from its first place of manufacture, has also been used. This method of preparation has now been given up entirely.



If a solution of ferrous sulphate, or any other ferrous salt, is treated with an alkali, a precipitate of ferrous hydroxide,  $\text{Fe}(\text{OH})_2$ , is formed. This precipitate is white in the pure condition, but takes up oxygen so easily, changing to a greenish black in color, that the white form can be made only under special conditions. The atmospheric oxygen dissolved in the solution is usually enough to darken the precipitate. The corresponding anhydride, ferrous oxide,  $\text{FeO}$ , is black and is also readily oxidized.

Hydrogen sulphide does not precipitate acid solutions of ferrous salts, because ferrous sulphide dissolves in acids (p. 215). With alkaline sulphides, a greenish-black precipitate of hydrated ferrous sulphide is formed, which soon oxidizes in the air to ferrous sulphate and basic ferric sulphate. A more stable, anhydrous form of ferrous sulphide,  $\text{FeS}$ , is made by placing some sulphur in a crucible and introducing a stick of iron heated at one end. The two elements unite with a strong evolution of heat, and by pushing the rod farther into the crucible and adding more sulphur, a large amount of the compound can be made. Ferrous sulphide is used in making hydrogen sulphide (p. 215), and is a black, slightly lustrous mass. Pyrite,  $\text{FeS}_2$ , is a sulphide that is commonly found in Nature. It contains twice as much sulphur but the combining proportions here do not correspond to any oxygen compound. Pyrite occurs as brass-yellow, metallic cubes and other crystalline forms of the isometric system. Perfectly developed crystals often occur in coal. Iron pyrites is one of the chief sources of the sulphur used in making sulphuric acid. It is roasted in the air, causing sulphur dioxide to pass off and leaving ferric oxide behind.

**265. Ferric compounds.** — Ferric compounds range from yellow to brown in color. Ferric chloride, the best known of these compounds, crystallizes with  $6 \text{H}_2\text{O}$ , and comes on the market in moist brown masses. It dissolves freely in water, giving a yellow solution with medicinal and technical uses. It is made by dissolving ferric oxide in hydrochloric acid; or iron is dissolved in hydrochloric acid and the resulting ferrous chloride oxidized with chlorine.

Alkalies or ammonia give with solutions of ferric salts a brown precipitate of ferric hydroxide,  $\text{Fe}(\text{OH})_3$ . This hydroxide occurs in large amounts in Nature and is the source of an important iron ore, limonite, sometimes found in black lustrous masses, like clusters of grapes. On heating ferric hydroxide, water is given off leaving behind the anhydride, ferric oxide, as a reddish-brown powder. It is bright red to dark violet in color according to the temperature of heating, and, as "rouge," is used to polish metals and glass and also as a pigment.

Ferric hydroxide, mixed with clay and other substances, often occurs in Nature as a residue from the weathering of silicates rich in iron, or as a deposit from waters that contain iron. The mixture is more or less strongly colored yellow, or yellowish brown, and is used under the name of *yellow ocher* as a cheap and durable pigment. Just as the hydroxide prepared artificially loses its water on heating and changes to red iron oxide, so likewise all varieties of ocher turn red on "burning" and as "burnt ocher" are also used as pigments. Pure ferric oxide when used as a pigment is called *caput mortuum*, or death's head. This name was given to the residue from the iron sulphate used in making sulphuric acid (p. 320) because of certain conceptions of the alchemists.

The red color of burned earthenware vessels, tiles, etc., is due to ferric oxide and the yellow or brown color of rocks to the hydroxide.

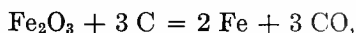
Iron oxide is also found as a mineral called *hematite*, which crystallizes in splendid rhombohedrons, isomorphous with corundum (p. 296). Other less crystalline forms are known as *red iron ore*. Some of these forms strongly resemble limonite but differ from it in their "streak"; *i.e.*, if the mineral is rubbed on a piece of rough porcelain a little powder, or a *streak*, is left, the color of which shows plainly against the white surface. The black masses of limonite give a yellowish-brown streak, while hematite gives a red one.

Finally there is found in Nature a compound of ferrous and ferric oxide,  $\text{FeO} + \text{Fe}_2\text{O}_3 = \text{Fe}_3\text{O}_4$ , which because of its magnetic properties is called magnetic oxide of iron, or *magnetite*, and which

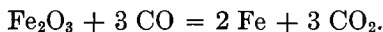
crystallizes in the isometric system. It is an iron-gray, somewhat metallic-looking mineral and is a valuable iron ore.

**266. Metallurgy of iron.** — For the technical production of iron, which is one of the most important of industries, only the oxide ores need to be considered. In addition to those already named (limonite, hematite, and magnetite) is ferrous carbonate,  $\text{FeCO}_3$ , called *siderite* or *spathic iron ore*, a mineral crystallizing in rhombohedrons isomorphous with calcite. All of these ores change to ferric oxide when heated, so that chemically speaking we are dealing with only one substance.

The production of iron from its oxides is based on the reducing action of carbon; two different reactions occur, depending on the conditions. On the one hand, iron oxide can be reduced by carbon with the formation of carbon monoxide,



and on the other hand, the carbon monoxide itself can act as a reducing agent,<sup>1</sup>



The temperature determines which reaction takes place; the first goes at the higher and the second at the lower temperature.

This makes the process of iron smelting easy to understand. Alternate layers of iron ore, carbon (coke) and fluxes are thrown into the top of a tall, egg-shaped furnace, the *blast furnace*, and air is introduced near the bottom. The coke in the lower part, where the temperature is highest, acts on the iron oxide in the sense of the first equation, while in the higher, cooler region of the furnace a part of the carbon monoxide also helps in the reduction. The rest of the carbon monoxide escapes unburned. This formerly produced a great flame at the top of the furnace, the "throat"; but at present the gas is piped off and burned where its heat can be utilized. Besides acting as reducing agent, a part of the carbon burns to produce the high heat needed for the smelting. The highest temperature is reached at the lower part of the furnace where the compressed air is forced in. The iron melts after combining with the excess of carbon present, and collects

as a liquid in the base of the furnace, where it is tapped off from time to time.

The crude iron made in this way is a cast iron, *i.e.*, it is rich in carbon. Occasionally castings are made directly from the blast furnace, but as a rule it is poured into so-called "pigs," which are afterwards remelted and worked into other forms of metal.

Pig iron contains carbon and, in addition, silicon and traces of sulphur and phosphorus, in quantities depending on the purity of the ore. The last two are injurious to the iron and must be avoided or removed. The percentage of carbon must also be reduced if other kinds of iron are to be made.

All this is accomplished by heating the iron till it melts and then exposing it to the action of the air to oxidize the impurities. There are two processes for accomplishing this, puddling and Bessemerizing, chemically the same, but differing in the mechanical details. The last method, named from its inventor, Bessemer, is the most important, as it effects the quickest and most complete purification. The molten pig iron is put in a pear-shaped vessel with fireproof lining, and air is blown through it. The oxidation of the carbon and silicon raises the temperature and the reaction is finished in a short time. The carbon is more or less completely burned off, depending on the properties sought, and the resulting product is *Bessemer steel* or *ingot iron*; the latter is similar to malleable iron. If the iron contains phosphorus, the interior of the Bessemer converter is lined with bricks of magnesia or lime. The phosphorus forms a phosphate and passes into the slag, so that a good quality of iron is produced. The formerly worthless phosphoric ores are made useful in this way, and at the same time agriculture is supplied with a good phosphate fertilizer, which has been called *Thomas slag* after the inventor of the method. This is again an example of an ideal technical process in which the by-product is utilized.

### § 37. MANGANESE.

**267. The metal.** — The element manganese closely resembles iron. The metal is lighter colored, with a somewhat reddish luster. It is almost never used in the pure state. It can be made

by the reduction of the oxides with aluminium (p. 297). It dissolves in acids more easily and quickly than iron does and in this respect resembles magnesium. Alloys of iron and manganese are used in the iron industry, as the manganese is useful in the Bessemer process because of its great heat of combustion. It also helps in the production of white cast iron.

**268. Compounds.**—Manganese is especially characterized by its power to form compounds in which the metal shows five distinct valences. The bivalent form resembles magnesium; the trivalent, aluminium; the quadrivalent, tin; the hexavalent is like sulphur in sulphates; and the heptavalent is like chlorine in perchlorates. Only a few of the typical compounds will be studied.

The metal dissolves in acids and forms pink salts of bivalent manganese which are of no particular value. Alkalies precipitate salmon-colored manganous hydroxide,  $\text{Mn}(\text{OH})_2$ , from the solutions. This compound oxidizes in the air to the brown trivalent manganic hydroxide, though not so quickly as in the case of the corresponding iron compound. In contrast to ferrous salts, neither dissolved nor crystallized manganous salts oxidize in the air. The only mineral in this group is manganese carbonate, or rhodochrosite, isomorphous with calcite.

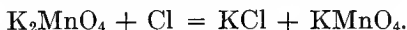
Trivalent manganese forms a brown manganic hydroxide, which may be obtained as just described. It is an extremely weak base, so that its salts are almost impossible to make because they readily undergo hydrolysis (p. 298). Manganese occurs in Nature in the trivalent state as a hydrated oxide,  $\text{MnO}(\text{OH})$ , in the form of black crystals with a brown streak; its formula can be derived from the hydroxide with loss of water.

The oxygen compound of tetravalent manganese,  $\text{MnO}_2$ , is the pyrolusite which has been frequently mentioned. It is a neutral substance, *i.e.*, does not show basic or acid properties, and is called *manganese dioxide* or *manganese peroxide*. It can, however, be assumed to be the anhydride of a very weak acid,  $\text{H}_2\text{MnO}_3$ , as a number of compounds are known the composition of which shows them to be salts of such an acid. They are called *manganites* and are brown or black in color.

269. **The acids of manganese.** — If sodium or potassium carbonate is melted with any oxide of manganese, a greenish-colored mass is formed. The coloration is so strong that a large amount of manganese colors the melt black and even slight traces are shown by the bluish-green tint. The reaction is used for the detection of manganese. The fused mass dissolves in water with a green color and contains a manganate, *i.e.*, a salt with the symbol  $K_2MnO_4$ , or  $Na_2MnO_4$ . The formula is like that of a sulphate. The manganates also crystallize in the same form as sulphates, so that the two acids are said to be isomorphous.

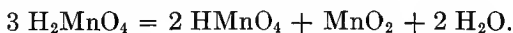
If the dark-green solution of a manganate is kept for a time in an open vessel, the color changes through blue and violet to purple. Because of this apparently spontaneous color change, the older chemists called the green solution *chameleon*. The color change takes place instantly if an acid is added. A purer color is obtained by the addition of a little chlorine or bromine water.

The reason for the change is the formation of a salt of a new acid, *permanganic acid*, the salts of which are called *permanganates*. The reaction takes place according to the equation



The new salt, *potassium permanganate*, differs from the manganate in having one combining weight of potassium instead of two; the corresponding acid, therefore, has the symbol  $HMnO_4$ . The purple color is due to the permanganate ion,  $MnO_4$ .

The reason that the color change is produced either of itself or by acids in the absence of chlorine or bromine, must now be explained. Free manganic acid is an unstable substance; when set free, it decomposes into permanganic acid and manganese dioxide according to the equation



Whereas all the manganese goes over to permanganate when treated with chlorine, in this case one-third is precipitated as the hydrated dioxide and the brown precipitate makes the solution

turbid. The reaction goes so easily that even the atmospheric carbonic acid will cause it. This is the reason that the change takes place in the air, though slowly.

Potassium permanganate is so strong an oxidizing agent that it is made in large quantities, by either the above method or by an electrolytic one, and has numerous technical uses. It forms glistening, violet-brown, almost black crystals which even in small quantities give a beautiful purplish-red solution. The crystals are isomorphous with those of potassium perchlorate,  $\text{KClO}_4$ .

## CHAPTER XII.

### HEAVY METALS OF THE COPPER GROUP.

#### § 38. LEAD.

**270. The metal.** — Metallic lead has been known for a long time. It is characterized by its great density (11.4) and its softness. It melts at  $330^{\circ}$ , and even in the solid state can be pressed easily into any desired form. Its industrial use depends in the first place on its density, which makes it suitable for shot and bullets, because the energy of motion is proportional to the weight. Its second use is based on its resistance to chemicals. It oxidizes easily, to be sure, but the attack is wholly on the surface. This is because most lead compounds are very slightly soluble and form a semi-permanent coating which protects the metal beneath.

Water pipes are often made of lead, for although pure water acts strongly on the metal in the presence of atmospheric oxygen, the soluble sulphates and carbonates found in ordinary water soon form an insoluble lining which prevents further action. For exactly the same reason, the lead chambers in the sulphuric acid plant resist the action of nitric and sulphuric acids, at least so long as the sulphuric acid does not get too concentrated, in which case the lead sulphate dissolves and the protective coating is no longer present.

Polished lead can be kept only a very short time in the air and is grayish white with a metallic luster. It soon changes to a dark gray, due to the very thin coating of oxide.

Large amounts of lead are used in making alloys. The easily fusible soft solder and type metal are examples of such alloys.

**271. Lead compounds.** — Lead is very simple in its chemical behavior and resembles the alkaline earth metals, particularly



barium, with which it is isomorphous in numerous compounds, and it also shows many corresponding solubility relationships. It behaves for the most part like a bivalent element, though it occasionally forms quadrivalent compounds. It is not soluble in dilute acids. Its compounds are generally made from the oxide which forms easily when the metal is heated in the air.

*Lead oxide*,  $\text{PbO}$ , commonly called *litharge* (the name arises from the fact that it occurs as a by-product in the smelting of silver) is a reddish-yellow substance, crystallizing in the form of indistinct scales. It is insoluble in water, but will dissolve in acids which form soluble lead salts, namely nitric acid and acetic acid.

*Lead nitrate*,  $\text{Pb}(\text{NO}_3)_2$ , is a white salt, crystallizing in the isometric system, and is isomorphous with barium nitrate. On heating it decomposes into lead oxide, nitrogen peroxide, and oxygen (p. 235). The solution gives with alkalies a white precipitate of lead hydroxide.

*Lead hydroxide*,  $\text{Pb}(\text{OH})_2$ , because of its weakly acid properties, is soluble in an excess of alkali. Sulphuric acid, and the sulphate ion in general, precipitates white, insoluble *lead sulphate*,  $\text{PbSO}_4$ , which is also found as the mineral anglesite. The crystals are isomorphous with those of barite.

Alkaline carbonates throw out from lead solutions insoluble, white *lead carbonate*,  $\text{PbCO}_3$ , also found in Nature as the mineral cerussite. It is isomorphous with aragonite and witherite and is a valuable lead ore.

*White lead* is a double compound of hydroxide and carbonate and is a pigment of great covering power. It is often made even to-day according to the old Dutch process, in which sheets of lead are placed in jars containing a little acetic acid and packed in moist tanbark or manure. The latter substances furnish carbonic acid, which, in the presence of acetic acid and atmospheric oxygen, attacks the lead and changes it to the basic carbonate. Various other processes are in use, but only those which furnish the basic carbonate instead of the neutral salt are of value.

White lead has two bad qualities in addition to its good ones.

First, it darkens with hydrogen sulphide because of a surface change to dark-brown lead sulphide. Secondly, it is poisonous like all lead compounds and produces exceedingly dangerous cases of poisoning in the factories where it is made, unless it is carefully handled. The first symptoms of lead poisoning are violent abdominal pains (lead colic), and paralysis finally results. Many attempts have been made to replace white lead with other substances, zinc white, for instance, and even less durable materials are used to avoid the danger of lead poisoning. It is all the more dangerous because lead belongs to the class of cumulative poisons and so may cause long-extended sicknesses.

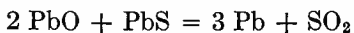
*Sugar of lead* is the soluble lead salt most commonly used. It is lead acetate,  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 + 3 \text{H}_2\text{O}$ , and is made by dissolving lead oxide in acetic acid. Its name comes from its sweetish taste. It dissolves in water, though it often forms a turbid solution because the acetic acid has been partly replaced by carbonic acid from the air, so that the salt has become covered with a layer of insoluble carbonate.

If lead oxide is cautiously heated in the air, it takes up oxygen and changes to a brilliant red powder, *minium* or *red lead*, of the composition  $\text{Pb}_3\text{O}_4$ . Red lead is used as a pigment and also in certain kinds of cement. If red lead is treated with dilute sulphuric acid, it decomposes into lead oxide which dissolves in the acid, and lead peroxide,  $\text{PbO}_2$ , which is left behind as a dark brown powder. The latter is obtained pure by washing and drying.

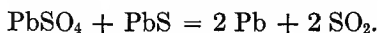
From solutions of lead salts which are not too strongly acid, hydrogen sulphide precipitates brownish-black lead sulphide,  $\text{PbS}$ , which, because of its dark color, can be recognized even in small quantities. The reaction is used not only as a test for lead, but also for detecting hydrogen sulphide, either by its action on lead solutions or on paper soaked in lead acetate. Very small quantities can be identified in this way.

**272. Metallurgy.**—Lead sulphide occurs abundantly in Nature in the form of heavy, metallic cubes: in this form it is called *galena*, which is the most important lead ore. To prepare lead

from it, the ore is first roasted, whereby it is converted into lead oxide and lead sulphate. The final reduction can be made either by carbon or by unoxidized sulphide. If the roasted product is heated with galena the following reactions take place:



and



In both cases metallic lead and sulphur dioxide are formed, the lead sulphide acting as a reducing agent towards the oxygen compounds.

Crude lead usually contains silver, from which it must be separated. Formerly, the separation was effected almost exclusively by taking advantage of the difference in behavior of the two heated metals toward oxygen. The lead is melted in a flat, circular furnace, the cupelling furnace, and oxidized by a current of air; part of the resulting lead oxide volatilizes and part of it is absorbed by the bed of the furnace. The silver is left in the metallic condition, and at the instant when the last of the lead oxidizes, the film of litharge breaks, showing a brilliant flash of colors (silver "blick"). More economical methods are now used. The crude melted lead is mixed with zinc, which does not alloy with the lead but floats on the surface as oil does on water. It takes the silver with it, however, so that on cooling, the hardened layer of zinc which contains the silver can be lifted off. The zinc is oxidized off by heating in steam, and pure silver is left. Another process depends on the fact that pure lead crystallizes first when lead containing silver is melted and allowed to cool, just as pure ice separates from a salt solution. The crystals are ladled out with a perforated ladle, and by systematic crystallization the mother liquor, rich in silver, can be separated from the lead crystals that are free from silver. The mother liquor grows richer in silver up to a definite concentration at which silver begins to separate. The lead rich in silver is treated as described above.

## § 39. COPPER.

**273. The metal.** — The knowledge of copper, as of gold and silver, dates back to the earliest times, because like those metals it is often found uncombined and is noticeable because of its red color. It does not belong to the noble metals, but resembles them to a certain extent, for although it is soon covered with a layer of oxide when exposed to the air, the coating is only superficial and is not followed by any serious corrosion even after a long time.

Pure copper is rosy red; this color can be seen if a piece of the metal is treated with hydrochloric acid to remove the thin surface coating. The color soon changes in the air to a much darker brownish red, the ordinary "copper red." Long exposure to moist air forms a green coating of basic copper carbonate (or under certain conditions the oxychloride). Antique objects made of bronze, an alloy of copper, usually show this "patina" which has been formed during long contact with moist earth; it is easily possible to make a similar coating artificially and in a short time.

Copper has, in its salts, the valences one and two; in the first series it acts like silver and in the second like ferrous iron. The second series is best known because most of the univalent compounds are changed by contact with air to the bivalent form. The latter form, therefore, will be considered first.

Copper will not evolve hydrogen when treated with acid. Hydrochloric acid will dissolve it slowly under the influence of atmospheric oxygen; concentrated sulphuric acid and dilute nitric acid will also dissolve it, the former on boiling and the latter in the cold, but the acids are reduced in both cases. A part of the sulphuric acid changes into sulphurous acid, which escapes as sulphur dioxide when copper turnings are heated with it. Nitric acid attacks copper more easily in proportion to the amount of the lower oxides of nitrogen that it contains. Absolutely pure nitric acid seems at first to be without action upon copper. Solution begins to take place after a time, however, and goes on with increasing speed. As soon as the first trace of copper dissolves,

the corresponding amount of lower oxide is formed and acts as a catalyzer. The reaction becomes increasingly violent.

**274. Copper sulphate.** — Copper sulphate,  $\text{CuSO}_4 + 5 \text{H}_2\text{O}$ , formed by the action of sulphuric acid on the metal, is a salt which dissolves in water forming a greenish-blue solution. It is formed from the natural sulphide by the action of water and oxygen, and for this reason it has been known for a long time. It is also called *blue vitriol* or copper vitriol. It crystallizes in forms which have absolutely no axis of symmetry. Its regularity is then limited to the fact that for each surface there is an opposite parallel surface. The corresponding crystal system is called the triclinic system.

Copper sulphate loses its water of crystallization on heating and changes over to a dirty white, powdery mass, which absorbs water again with great ease and shows the hydration by the return of its blue color. It can, therefore, be used for drying nonaqueous liquids, *i.e.*, freeing them from dissolved water, and if a fresh portion of the dehydrated salt stays white it shows that the dehydration of the liquid is complete.

An aqueous solution of copper sulphate loses copper when brought in contact with zinc or iron, and changes to the corresponding salt of the other metal. The noble and base metals form a series based on a similar behavior; silver salts are precipitated by copper, copper salts by lead, lead salts by iron and zinc, and in each case the less noble metal replaces the nobler one in the solution. Ferrous salts ought, theoretically, to be precipitated by zinc, but in this case water prevents the action by oxidizing the iron. The series stops at this point because the other metals, particularly the light metals, cannot exist in water since they decompose it.

This process has a certain historical interest. Solutions of copper sulphate form readily wherever sulphide copper ores are exposed to moist air. Thus it was noticed in different mines that certain mine water apparently had the property of changing iron into copper. It is well known that during the Middle Ages the alchemists tried in vain to make gold out of the baser metals. We know now that this contradicts the law of the conservation

of the elements; at that time, however, the change described above was taken as conclusive proof that *transmutation*, or the change of one metal into another, was perfectly possible. This shows the way in which correct observations have led to mistakes because of false assumptions. It is perfectly true that in the place where the iron was at first copper was found. As we now know, this did not come from the iron but from the mine water, by which the iron was dissolved and carried away.

**275. Electrolysis.** — If an electric current (*e.g.* from a dry cell) is allowed to pass through two copper plates, which, without touching one another, are kept parallel to each other in a saturated copper sulphate solution, it is found that metal dissolves from one plate and is deposited upon the other. The two quantities of copper, that which is dissolved and that which is deposited, are equal and they are *proportional to the quantity of electricity which has passed through the copper solution*. This is so exact that the apparatus can be used to measure the amount of current by weighing the copper plates after a definite time and from the increase in weight of one of them the amount of current that has passed during this time can be calculated.

The copper plate which is joined to the zinc of a galvanic element increases in weight, while the other copper plate loses; the former, to which the copper goes, is called the *cathode*, the other, from which it dissolves, is the *anode*. The positive current enters the solution at the anode and passes to the cathode; the copper, therefore, moves with the positive current. The sulphate ion,  $\text{SO}_4$ , moves in the opposite direction; the anode dissolves simply because the  $\text{SO}_4$  combines with its copper, forming new copper sulphate and in exactly the same amount as that used up at the cathode due to the deposition of copper. For this reason, the current can be passed through the solution as long as some of the anode remains undissolved, and the solution will always contain the same amount of salt.

**276. The ions.** — A satisfactory conception of what happens is reached if we assume that the copper atoms in the solution are charged with positive electricity, the  $\text{SO}_4$  groups with negative electricity, and that by their passage in opposite directions

a current is produced. This is the reason they have been called *ions*, *i.e.*, wanderers. Copper which migrates to the cathode is a *cation*, and  $\text{SO}_4$  which migrates to the anode is an *anion*. As the bivalent copper compounds are called cupric compounds, the copper ion is called the cupric ion; the name sulphate ion for  $\text{SO}_4$  is already known.

We know that if we assume the existence of atoms we must also assume that all the atoms of the same substance are alike. It follows, too, that the electrical charges on all copper ions must be equal, or else the quantity of copper separated could not be proportional to the quantity of electricity transported. Moreover, the negative charge of the sulphate ion must be equivalent to the positive charge of the copper ion. The solution contains the same number of ions of each kind, as copper sulphate contains the same number of copper ions that it does of sulphate ions. If, for example, the negative charge of the latter were greater than the positive charge of the former, copper sulphate and its solutions would show a negative charge, corresponding to this excess. As this is not the case, the charges are necessarily equal.

Still further deductions can be made. Cupric nitrate is electrically neutral. It contains the same copper ion as the sulphate, and so it follows that two nitrate ions together have the same negative charge as a single sulphate ion. The same is true for all other anions that can form cupric salts. On the other hand, the sulphate ion can form neutral salts with all cations; the positive charges of all these cations must also be equal. One atom of a bivalent metal or two atoms of a univalent one combine with a sulphate ion; it follows from this that *the electrical charges of the ions are proportional to their valence*. If the charge carried by one atom of a univalent cation is called  $F$ , then  $-F$  is the charge of a univalent anion and  $nF$  or  $-nF$  is the charge of an  $n$ -valent cation or anion.

A remarkable conclusion may be drawn from these considerations. If the same current is sent through a series of decomposition cells arranged like that described for copper sulphate, the same amount of electricity passes through each cell, as the

same current goes through them all. Then the different metallic masses must deposit on the different cathodes in quantities which bear the same relation to each other as the atomic weights of the elements concerned, divided by their valences. If these quantities are called *equivalent*, the law reads that the same current deposits in the decomposition cell equivalent quantities of different metals. If, for instance, a current is passed through a circuit containing a copper cell and a silver cell until 107.88 g. of silver have separated, the quantity of copper will be  $63.57 \div 2 = 31.79$  g. As a matter of fact this is so exact that the relations of the equivalent and combining weights of copper and silver have been determined in this way.

This important law, that *equivalent quantities of all ions transport equal quantities of electricity*, is called Faraday's law, after its discoverer. It was first discovered in a purely empirical way when Faraday proved by experiment that these weight relations held true. Later the line of reasoning shown above was suggested, and it became evident that it was a necessary consequence of the empirical law that free electricity is never produced by the reactions of salts (or chemical substances in general). This fact had been known for a long time and also the fact that in conductors of the second class, or *electrolytes*, the current is carried with the aid of the chemical components or ions. Faraday's direct observations, however, were the first to lead up to the law. Up to that time no one had the courage and insight to draw such far-reaching conclusions from the material at hand. And even if it had been done earlier, the law would not have been accepted as true until it had been established by experiment. Errors can be made much more easily in theoretical speculation than in direct experimentation and hence the fact that properly conducted experiments are indispensable.

**277. Voltaic cells.** — The reverse phenomenon of the production of electrical energy from chemical energy is also based on Faraday's law. By causing ions to form and disappear under the influence of chemical action in such a way that a movement of electricity necessarily takes place, a current can be produced which has its source in chemical energy.



The experiment on page 333 in which a copper sulphate solution is so acted on by zinc that zinc sulphate and copper are formed, will serve as an example. If the zinc is simply put into the copper solution, a chemical reaction takes place and free energy appears as heat. With the following arrangement, on the contrary, the reaction cannot take place without producing an electric current. Partly fill a glass vessel with zinc sulphate solution and place a stick, or plate, of zinc in the liquid. This of course is unattacked by the solution. Next put in the glass a porous earthenware cylinder and into it pour some copper sulphate solution. Place a copper plate in this second cup. Attach each of the two metals to a wire and lead the two wires through an electric bell or other signaling apparatus: a current is produced and the bell rings. The reason is this: zinc has a tendency to go into solution and form a salt (*i.e.*, it seeks to form a zinc ion), and this tendency is so great that it can force copper ions out of solution. Between metallic zinc and the zinc ion there is the difference that the latter carries the charge,  $2 F$ ; the same is true for copper and the copper ion. From this point of view the precipitation of copper from its solution by zinc is because the latter takes the electrical charge from the copper; the sulphate ion remains unaffected. The same tendency exists in the system just described, which is called the Daniell cell in honor of its inventor. Zinc goes into solution and copper is forced out. In order that the zinc can change to the zinc ion it must pick up a charge of  $2 F$ . It takes this charge through the metallic conductor from a copper ion that is in contact with the copper plate; thereby the ion is changed to uncharged metallic copper, which is deposited on the plate. The reaction can take place only when the circuit is closed, but will continue as long as metallic zinc and copper ions, *i.e.* copper sulphate, are present in circuit. Both are used up in the process and so furnish the work needed to keep up the current. The sulphate ion does not undergo any loss; for whereas it is combined first with the copper ion to form copper sulphate, later on it forms zinc sulphate with the newly formed zinc ion.

It is evident that the cell produces electrical energy only

because of the chemical reaction; the action of zinc on copper sulphate is separated into two stages in such a way that the two steps of the reaction occur in different places connected only by the electric current. The current must necessarily flow whenever the chemical reaction takes place, and if one is stopped the other also stops.

The various chemical combinations used in galvanic<sup>1</sup> cells, or elements, are all based on the general principle outlined above. It is not necessary that the chemical process which causes the current shall always be the precipitation of a metallic salt by another metal; on the contrary, every chemical reaction in which ions are in any way concerned can be made to produce an electric current. The details of the different methods form a special division of science, *electrochemistry*.

**278. Other copper salts.**—Copper sulphate, or blue vitriol, is used in large quantities and for various purposes, — in medicine, in dye work, in making galvanic cells, etc.

Of the other copper salts, the chloride,  $\text{CuCl}_2$ , should be mentioned. It crystallizes with  $2 \text{H}_2\text{O}$  in needles which are usually grass green but when perfectly pure are bluish green. When the salt is dehydrated it does not become white like copper sulphate but dark brown. The same color is seen when the hydrated salt is dissolved in concentrated hydrochloric acid. If the solution is diluted with water it turns first yellow, then green, becoming more and more blue until it finally has the color of the other copper salts. This is because the yellowish-brown color of the anhydrous salt is most marked in a concentrated solution, so that the blue becomes greener and yellower with increasing concentrations.

If words are written on paper with a solution of copper chloride (a steel pen must not be used) the writing is hardly visible. If the paper is heated, the brown anhydride is formed and the writing appears yellow or brown. The color disappears again

<sup>1</sup> Volta shares with Galvani the honor of having discovered the means of producing an electric current at the expense of chemical action upon one of two united plates of dissimilar metals. The words *voltaic* and *galvanic* are therefore synonymous.

on standing in the cold, because the salt adds water and goes back to the pale green form. Reactions of this kind used to arouse a great deal of interest, and the copper chloride solution was used as a "sympathetic ink" which could be seen only by those who knew the secret.

The carbonates of copper are of some importance. Precipitation with an alkaline carbonate from an aqueous solution produces a basic salt of a greenish color. A normal copper carbonate does not occur in Nature, but two basic compounds of carbonate and hydroxide are known. The first is dark blue and is called *azurite*; its powder is used as a pigment under the name *mineral blue*. The other is a vivid green and is known as *malachite*. Both are used for decorative purposes if they are well formed, and otherwise as copper ores.

Soluble bases throw down from cupric solutions a precipitate of copper hydroxide, light blue in color. On moderate heating, the hydroxide in contact with the liquid goes over to its anhydride, copper oxide, and turns black. The same oxide is formed when metallic copper is heated in the air, and as it breaks off when copper is worked under the hammer it is sometimes called *hammer scale*.

Ammonia also precipitates the hydroxide at first; if an excess is added, however, a dark-blue solution is formed which is perfectly clear and totally different and much deeper blue than ordinary copper solutions. This shows that a new substance has been formed. The corresponding dark-blue salt can be precipitated by alcohol from the ammoniacal solution and differs from the original copper salt by containing 4  $\text{NH}_3$  and only 1  $\text{H}_2\text{O}$ . The ammonia, then, has combined with the cupric ion to form a new ion,  $\text{Cu}(\text{NH}_3)_4$ , called the cupri-ammonium ion, and to this is due the blue color. The color change is so striking that it can be used for the detection of cupric compounds.

Hydrogen sulphide precipitates black, hydrated copper sulphide,  $\text{CuS}$ , which in the anhydrous condition is found in Nature as the rare mineral covellite. The compound is unstable, easily loses half of its sulphur and goes over to the cuprous sulphide,  $\text{Cu}_2\text{S}$ , which will be described later.

**279. Cuprous compounds.** — Cuprous oxide,  $\text{Cu}_2\text{O}$ , is the most important compound of univalent copper. It is a red substance, crystallizing in octahedrons, and is the richest of the copper ores. The mineral is called *red copper ore* and is easily reduced by carbon to metallic copper.

Cuprous chloride,  $\text{CuCl}$ , is made by dissolving cupric chloride in strong hydrochloric acid and adding copper turnings. As much more copper dissolves as was originally present. The solution is first dark brown, then bright yellow; the hydrochloric acid now holds in solution the cuprous chloride, which is difficultly soluble in water. If the hot solution is poured into a large excess of cold water, the cuprous chloride deposits as a white crystalline precipitate. This dissolves in ammonia, giving a colorless solution, but it soon takes up oxygen from the air and changes to the corresponding cupric compound, as the deep blue color of the copper ammonium salt shows.

**280. Metallurgy.** — Cuprous sulphide occurs as a mineral and is called *chalcocite* or *copper glance*. It is a valuable copper ore. Chalcopyrite, of the composition  $\text{CuFeS}_2$ , is of more common occurrence.

To get metallic copper from its sulphide ores, they are first roasted to oxidize part of the sulphur, after which the product is melted and another part of the sulphur is removed as sulphur dioxide. The roasting and melting are repeated and the crude copper is then used as an anode in a copper sulphate solution, the cathode being a plate of pure copper. The copper migrates to the cathode as described on page 334; the impurities either sink to the bottom as an insoluble slime or else dissolve in the liquid without depositing on the cathode. Electrolytic copper is very pure, a matter of great importance in the use of copper for electrotechnical purposes. This is due to the fact that of the cheaper metals copper is by far the best conductor and, therefore, carries the current with the least loss. The conductivity is greatly reduced by slight traces of impurities, so that electricians now use a much purer copper than was formerly available. Electrical science, because of its own development, has made possible an electrolytic purification process by means of which an

exceedingly pure and highly conducting copper can be produced at moderate expense.

**281. Alloys.**—Copper is also used in the preparation of articles like coins, which require a certain chemical and mechanical durability. Many alloys of copper have been used. Brass, or copper-zinc, has already been mentioned. Copper with 10 per cent aluminium makes a valuable alloy, aluminium bronze, which has a golden yellow color and a high resistance to chemicals and to mechanical strain. Tin forms with copper sculptor's bronze and bell metal. The "ore" of the old writers is a copper alloy containing zinc, lead, and tin, besides copper. It is not made from the metals but is formed by smelting the mixed ores with coke, and for this reason its composition varies largely with its source.

#### § 40. MERCURY.

**282. The metal.**—Mercury, or "quicksilver," also belongs to the metals known by the ancients because it occurs in Nature as the free element and because its contradictory properties, fluidity and metallic character, early attracted the attention of investigators. When, in addition, its volatility was discovered, a property then unknown in other metals, it was held to be a most mysterious and important element. The alchemists of the Middle Ages called it mercury and considered it the type of all metals and the principle of all metallic properties. It gained still greater prominence later when its pronounced medicinal properties were discovered, and to-day it is an indispensable aid in physical and chemical work (the thermometer, barometer, and mercury bath should be recalled) and has contributed largely to the development of science.

The properties of metallic mercury are well known. At  $-39^{\circ}$  it changes from its usual liquid form to a solid and is then malleable like silver. It boils at  $358^{\circ}$ , but vaporizes to a considerable extent even at room temperature. Its density is 13.595 at  $0^{\circ}$  and its combining weight is 200.0. It belongs to the noble metals inasmuch as it does not oxidize at ordinary temperatures; oxidation takes place slowly, however, at  $350^{\circ}$ .

If it becomes dull in the air it is impure, and can be purified by shaking violently with dilute nitric acid, which will dissolve the less noble metals. It is shown to be pure when it will run over paper or glass "without leaving a tail," *i.e.*, without leaving behind it a gray trail formed by drops which because of the impurities on their surfaces are extended backwards to a point.

Mercury dissolves many other metals by "amalgamating" with them. It acts in this way on gold, silver, copper, lead, and zinc, but not on iron, so that it can safely be brought in contact with iron apparatus. For the same reason it is usually shipped in iron bottles. It combines with the alkali metals with a marked evolution of heat, and the product hardens with a comparatively small amount of the alkali metal. Sodium amalgam, in particular, is used as a reducing agent, being much easier to handle than pure sodium. If a little piece of sodium, brightened by scraping off its outer surface, is put in a mortar containing mercury, pushed below the surface with a pestle and moved back and forth a few times, combination takes place with a hissing noise and occasionally with a flame. The resulting sodium amalgam generates hydrogen with water, but far less violently than metallic sodium. A reddish-yellow solution of ferric chloride is quickly decolorized by sodium amalgam and the iron is reduced to the ferrous state,  $\text{FeCl}_3 + \text{Na} = \text{FeCl}_2 + \text{NaCl}$ .

**283. Mercurous compounds.** — The compounds of mercury, like those of copper, are arranged in two series, a univalent mercurous series and a bivalent mercuric series. The two forms are about equally stable. If dilute nitric acid is poured over mercury, the latter is attacked, and after the acid has stood for some time in contact with an excess of metal, white crystals of mercurous nitrate,  $\text{HgNO}_3$ , begin to separate. This salt is not soluble in water without decomposition, but changes to a basic salt with a separation of free nitric acid. If, however, a little nitric acid is added at the start, a clear solution can be made. If a few drops of the solution are rubbed on copper, zinc, or brass, the mercury deposits on the surface and the metal takes on a brilliant silvery luster. Silver and gold are not attacked by such a solution, as they are nobler than mercury.

If hydrochloric acid, or a metal chloride (*i.e.*, a chloride ion), is added to the solution, a white, curdy precipitate of mercurous chloride,  $\text{HgCl}$ , is formed which looks much like silver chloride (p. 345). It can be distinguished from the silver salt because it turns black with potassium hydroxide, whereas silver chloride does not. The darkening is due to the fact that potassium hydroxide forms the lower oxide of mercury from mercurous chloride, but silver chloride is not decomposed in this way. The behavior with alkalis gave mercurous chloride its old medical name, *calomel*, which means black.

Calomel acts as a cathartic and is much used in treating children's diseases. It is a white, heavy, crystalline powder, practically insoluble in water. It volatilizes readily and condenses as brilliant crystals.

Mercurous oxide is a black precipitate obtained from mercurous nitrate by the addition of sodium or potassium hydroxide; it forms directly as the anhydride instead of as the hydroxide and has the composition  $\text{Hg}_2\text{O}$ . This substance, like almost all mercury compounds, has a medicinal use; it is unstable and decomposes readily into mercuric oxide and metallic mercury.

**284. Mercuric compounds.** — If mercury or mercurous nitrate is heated with an *excess* of nitric acid, the resulting solution does not show the property of being precipitated by hydrochloric acid. It contains *mercuric nitrate*,  $\text{Hg}(\text{NO}_3)_2$ , *i.e.*, the nitrate of the bivalent mercuric ion. This salt, too, will dissolve without decomposition only in dilute nitric acid; pure water precipitates a yellow basic salt. Addition of alkali causes the formation of a reddish-yellow precipitate, which is simply the well-known mercuric oxide,  $\text{HgO}$ , with the aid of which we learned the fundamental principles of chemical combination. As we know, this oxide decomposes on being heated into oxygen and mercury, both in the gaseous condition. The mercury condenses readily, while oxygen remains a gas.

Another important compound is mercuric chloride,  $\text{HgCl}_2$ , which is called in medicine *corrosive sublimate* or simply *sublimate*. It is a white, crystalline, easily sublimable substance, which dissolves in water slowly and not very freely. The

solution has a disagreeable metallic taste and is an active poison. It is poisonous to the lower and to the higher forms of animal life and in very dilute solutions (1: 1000) is used for "sterilizing," *i.e.*, it is used in surgical operations for washing instruments and the operator's hands in order to kill the tiny living things or germs which might be present. To avoid any danger that might come from accidentally drinking the poisonous liquid, the corrosive sublimate tablets, which are usually mixed with common salt to increase the solubility of the  $\text{HgCl}_2$ , are often colored with a dyestuff and give a colored solution.

Mercuric iodide,  $\text{HgI}_2$ , forms as a bright red powder when the two elements are rubbed together in proper proportions, or the reaction can be hastened by adding a little alcohol in which the iodine dissolves and which can be subsequently removed by evaporation. The iodide is soluble in alcohol but not in water. If an alcoholic solution is poured into water, the iodide is precipitated, coming down, however, not as a red precipitate but as a yellowish-white one which turns red again after a long time, and more quickly in the sunlight. This is because mercuric iodide is dimorphous, like sulphur. If the red powder is heated cautiously and with constant motion, it suddenly turns yellow at  $126^\circ$  or a little above. It also sublimes in the yellow form when heated in a test tube. The yellow crystals turn red again in the cold, though not instantaneously nor all at the same time. Ordinarily a few red points form and from these points, red patches extend and slowly increase in size.

#### § 41. SILVER.

**285. Silver nitrate.** — It has been stated (p. 228), that nitric acid is so strong an oxidizing agent that it can dissolve a noble metal like silver. The noble metals, in general, have so slight a tendency to form salts that they are unable to reduce the ordinary acids and set hydrogen free. The formation of their salts can take place only in the presence of an oxidizing agent.

Nitric acid is the reagent used in making silver salts. If metallic silver is treated with the acid, which should not be too

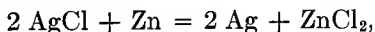


concentrated, solution takes place with generation of the well-known brown fumes. A very concentrated acid forms a coating of solid salt on the metal and protects it mechanically from further action; this salt coating will dissolve in dilute acid.

If pure silver has been used, the resulting solution is colorless. Common silver, such as is used for coins and silver articles, gives a blue solution because of the copper nitrate formed at the same time. Pure silver is too soft a metal to be used for commercial purposes which require that it must have a certain amount of durability; it is, therefore, usually "alloyed" with copper to harden it.

To get pure silver from a solution containing copper, hydrochloric acid is added. The solution contains silver nitrate, which, as silver is univalent, has the symbol  $\text{AgNO}_3$ . When hydrochloric acid is added, a white precipitate of silver chloride,  $\text{AgCl}$ , is thrown down at once and nitric acid is set free. Hydrochloric acid is added as long as a precipitate continues to form. Since silver chloride is insoluble, all the silver will be precipitated in this way, and as copper chloride is soluble it will all stay in solution. Brisk stirring collects the silver chloride in flocks like curdled milk, and this type of precipitate is for that reason known as "curdy." After standing, the supernatant liquid is poured off and fresh water is added to remove the remaining copper salts; the solution is again decanted and the process is repeated several times. The silver chloride is finally transferred to a filter and washed with water until the washings are no longer acid to litmus. The precipitate is then free from nitric acid and from copper salts.

Pure silver is made from the moist chloride by adding a little hydrochloric acid and introducing a piece of zinc. The following reaction takes place,



in which the chlorine leaves the silver and goes to the zinc. A gray powder of metallic silver is left, while the soluble zinc chloride goes into solution. The reaction is allowed to go on for several days in order that the transformation may be com-

plete; the progress of the reduction can be judged by the increase of gray color. Any undissolved zinc is removed. The moist silver can be treated directly with nitric acid, in which it dissolves readily. The colorless solution is cautiously evaporated and the excess nitric acid finally expelled by strongly heating (under the hood). A white salt is left, readily soluble in water and giving a solution which if dropped on the skin produces spots, colorless at first but soon turning black and becoming practically indelible. The salt is silver nitrate,  $\text{AgNO}_3$ ; the crystals are anhydrous and fuse easily to a colorless liquid.

In the process just described, the formation of the pure salt was based on the fact that in the solution, originally impure, the addition of hydrochloric acid caused the silver alone to form an insoluble substance, all the impurities remaining in solution. This made it possible to separate, by washing, the main substance, silver chloride, from the compounds associated with it. The silver chloride was then changed to silver by means of zinc, but again a soluble compound of the latter was formed and could be washed out. It is seen from this process how important to technical chemistry is the general idea that in the preparation of a pure substance a single solid form should be produced in contact with the liquid (dissolved) impurities. To find the conditions that must be fulfilled for this purpose it is necessary to know the solubility relations of various compounds, and here again we see the importance of a general scientific knowledge for practical technical operations.

The preparation of silver nitrate can be carried out in another and somewhat shorter way. If the blue solution containing copper nitrate and silver nitrate is evaporated to dryness in a porcelain dish and then heated till the salts melt, the copper nitrate decomposes with the evolution of nitrogen peroxide and oxygen, leaving copper oxide, a reaction exactly analogous to that of lead nitrate (p. 235). The mass becomes black, due to the copper oxide color. When the brown fumes have stopped forming, the mass is allowed to cool and then is treated with water. The undecomposed silver nitrate dissolves, while the insoluble copper oxide is left behind. It is only necessary to

filter the solution in order to get a pure neutral solution of silver nitrate.

The separation in this case depends on the different behavior of the two nitrates when heated. If the behavior of the individual substances at high temperatures had not been studied, this simple method of separation could not have been devised.

**286. Ionic reactions.** — A silver nitrate solution prepared in the above way is much used as a laboratory reagent. It has already been stated that on the addition of hydrochloric acid a precipitate of silver chloride is thrown down, which is white and forms curdy masses on shaking. This reaction is based on the fact that hydrochloric acid is the chloride of hydrogen, because the chlorine ion alone is concerned in the reaction. All other soluble chlorides behave in the same way. The experiment can be tried with common salt, potassium chloride, calcium chloride, magnesium chloride or any of the other chlorides that have been mentioned. The same white, curdy precipitate is always formed and the precipitate has the curious property of darkening to an almost slate-gray color in the sunlight. This phenomenon will be taken up in more detail a little later.

Silver nitrate solution, then, is a general reagent for chlorine whenever the latter is combined with a metal (or a group resembling a metallic element, as ammonium, p. 247) to form a salt. Chlorine combined in a salt of this type is called the chlorine ion, and a silver solution is therefore a general *reagent for chlorine ions*. It is immaterial what metal or what base is converted to the corresponding chloride, the resulting salt will always give the same white precipitate of silver chloride.

We have a similar behavior in the case of sulphuric acid and its salts, *i.e.*, with the sulphate ion (p. 210), in which case a solution of barium chloride is found to be a general reagent for sulphate ions. Experiment shows in the same way that every other soluble silver salt gives the same precipitate of silver chloride with chlorine ions. Silver combined in a salt is called the silver ion, and we can say in general that silver ions and chlorine ions give a curdy precipitate of silver chloride. This includes all cases which can occur, and says in addition that

it does not matter what ions other than silver and other than chlorine are present.

For this reason it is not at all necessary to know what ions, *i.e.* what other salts, are present in an unknown solution before making a test with the silver solution. If an unknown solution gives the white, curdy precipitate with silver nitrate, it is certain that chlorine ions are present in the solution. It has been found out in this way that all drinking water contains chlorine ions.

Similar insoluble precipitates with silver ions are also given by bromine and iodine ions, but these can be distinguished from the chlorine by their appearance and behavior with other reagents. Analytical chemistry considers these differences in detail.

**287. Photography.** — Silver chloride in the pure condition is a white substance which fuses readily and on cooling hardens to a dark-colored, tough mass, looking somewhat like horn and often called horn silver for this reason. It occurs as a mineral.

The most important use of silver chloride is in photography. Silver chloride darkens in the light, as has been stated. This is because a chemical decomposition has taken place; chlorine escapes or combines with other substances present and metallic silver separates in a very finely divided condition. This fine silver may deposit in various ways and in different colors, gray, black, brown, etc., according to the conditions of its formation. Take a piece of white paper and wet one side of it with a dilute sodium chloride solution (1:100), dry and then treat with a solution of silver nitrate (1:10); in this way a paper sensitive to light is prepared which must be dried in a dark room. Place the dry paper in a "printing frame" under a photographic negative, *i.e.*, a glass plate carrying a picture in which dark and light are reversed, and expose to daylight; the paper darkens most strongly where the negative is most transparent and stays white or light-colored where the negative is darkest. This produces a "positive," *i.e.*, a picture with light and shade in their true relations. When the picture is dark enough, it may be taken from the frame, but must not be kept in the light

until the excess of silver chloride has been removed. A solution of sodium thiosulphate (1:5) is used for this purpose. After treatment with this "fixing salt," wash the picture for a long time with cold water and then dry it. A picture made in this way is not particularly good. The silver from which the image is composed has a dull brown color and, moreover, has sunk into the paper fiber to such an extent that the details are not sharp. The technique of photography has been developed in many different ways so as to overcome all these difficulties, and the positive papers now on the market give splendidly clear pictures because the silver is held in an especially prepared gelatin film with which the paper is coated. The picture may also be "toned" by treating it chemically so as to replace the brown silver with other elements, especially gold and platinum, which give a better appearance.

In preparing negatives, plates of glass or other transparent material are coated with a mixture of silver bromide and gelatin. Even exceedingly short exposures to light change the silver bromide to such an extent that on treatment with a substance that withdraws bromine (the "developer") the bromide changes to silver much more quickly in those parts exposed to the light than in the parts not acted on. The image made by the camera lens is allowed to fall on a plate or film which is then treated with the developer in a dark room. When the picture has "developed," the excess of silver bromide is removed by sodium thiosulphate ("hypo"), and after washing and drying the negative is ready for use. Exposure and development must, of course, be carried out properly to insure good pictures.

Besides the process which has just been outlined there are many other methods, particularly for producing the positive. All of them depend on the fact that certain substances or mixtures are sensitive to the light, *i.e.*, that they undergo chemical change in the light. That this is possible can be understood when it is remembered that light, too, is a form of energy and therefore has the power to do work. It does chemical work with substances that are sensitive to light. The chemical work which light does in plants has already been discussed (p. 257).

**288. Other silver compounds.** — Silver nitrate is almost the only silver compound in common use. It is sometimes called by its old alchemical name, *lunar caustic*, and is very poisonous. The dark spots formed on the skin and on other organic substances in the light are due to metallic silver formed from the nitrate by the action of the organic material and of the light. The spots can be removed by touching them with chlorine water, forming silver chloride, which is in turn soluble in sodium thiosulphate.

If sodium or potassium hydroxide is added to a silver nitrate solution a brown precipitate of *silver oxide*,  $\text{Ag}_2\text{O}$ , results. Silver hydroxide,  $\text{AgOH}$ , would be expected in this case, but the compound is unstable, and even if it should form would decompose at once into its anhydride, silver oxide, according to the equation  $2 \text{AgOH} = \text{Ag}_2\text{O} + \text{H}_2\text{O}$ . After washing and drying, a brown powder is left which on heating decomposes into metallic silver and oxygen similarly as in the case of mercuric oxide (p. 98). A much lower temperature will cause the decomposition of silver oxide.

Hydrogen sulphide produces in silver solutions (even when they contain free acid) a brown precipitate of *silver sulphide*,  $\text{Ag}_2\text{S}$ . This occurs in Nature as argentite, sometimes alone and sometimes mixed with other sulphides. It is an important silver ore.

Metallic silver is so well known that no description of it is necessary. It melts at about  $1000^\circ$  and does not oxidize in the air under any conditions. In contact with compounds containing sulphur, particularly hydrogen sulphide, it blackens because of the formation of silver sulphide. This is the reason that silver spoons darken when they are left in contact with eggs, as the latter contain sulphur (p. 216). If a blackened spoon is dipped in dilute hydrochloric acid and then touched with a piece of zinc, it becomes white at once. This is due to the fact that under these circumstances an electric current is generated, which carries the sulphur from the silver to the zinc, leaving the former pure.

## CHAPTER XIII.

### TIN, GOLD, AND PLATINUM.

#### § 42. TIN.

**289. Tin.** — Tin occurs almost entirely as tin dioxide,  $\text{SnO}_2$ , called *tinestone* or *cassiterite*, which crystallizes in the tetragonal system. This system is characterized by the fact that it has three perpendicular axes, of which two are equivalent and the third different. The fundamental form, therefore, is an octahedron, one axis of which is long or short as compared to that of a regular octahedron. Looked at in the direction of this principal axis the figure is tetragonal, from which the system takes its name. The major axis is a quaternary symmetry axis, for as the two secondary axes are equal, a revolution through one right angle brings the figure into coincidence. Fig. 74 shows the simplest form looked at in the direction of the major axis.

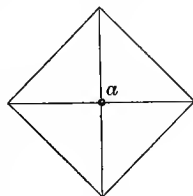


Fig. 74.

Tinstone commonly occurs as an inclosure in other rocks and is concentrated by a process of washing and settling the finely crushed ore. The tinstone settles first because of its greater density. Reduction with carbon takes place easily, giving the well-known white metal which keeps its luster for a long time in the air and in water and has been used for many years in the manufacture of *tinware*. Tin melts at  $235^\circ$  and oxidizes readily to tin dioxide, used as a polishing powder under the name "tin-ashes."

Because of its resistance to chemical action, tin is used in the form of thin sheets (tin foil) and in tubes for wrapping and inclosing food, oil paints, etc. Copper and iron dishes are often plated with tin to make them more resistant. *Tin plate* is sheet iron covered on both sides with tin. Tin alloyed with

lead gives a readily fusible metal, *soft solder*, used in joining brass and tin plate. With copper it forms *bell metal* and *bronze* and is of frequent occurrence in other metallic mixtures.

**290. Compounds.**—Tin forms two series of chemical compounds; in one, the stannous series, it is bivalent, and in the stannic series quadrivalent.

When tin is heated with hydrochloric acid, hydrogen is evolved and the tin dissolves, forming stannous chloride,  $\text{SnCl}_2$ . On evaporation a colorless salt containing 2  $\text{H}_2\text{O}$  is left that has a fairly extensive use in dye works under the name *tin salt*. It is used in the laboratory as a reducing agent because it changes readily to the stannic form. For example, an acid solution of tin salt will decolorize iodine solutions and it will precipitate mercurous chloride or even free mercury from a mercuric chloride solution.

Alkalies throw down white stannous hydroxide from stannous solutions. This also acts as a very weak acid and dissolves in excess of alkali, forming *stannites*, which are powerful reducing agents.

Hydrogen sulphide precipitates brown stannous sulphide,  $\text{SnS}$ , from stannous solutions.

Among the stannic compounds is the dioxide,  $\text{SnO}_2$ , which has been mentioned above. If metallic tin is heated in a stream of chlorine, stannic chloride,  $\text{SnCl}_4$ , is formed as a colorless *liquid* that boils at  $120^\circ$  and fumes strongly in the air because of its decomposition by water vapor into hydrochloric acid and stannic hydroxide,  $\text{Sn}(\text{OH})_4$ . It will dissolve in a large amount of water to a clear solution because stannic hydroxide, like silicic acid (p. 307), then remains in the colloidal form. A concentrated colloidal solution usually hardens to a jelly. With still less water a series of crystalline hydrates is formed. Stannic chloride is used in the dyeing industry in the hydrated crystal form.

The oxide is also formed when tin is oxidized with nitric acid. It is not dissolved but is left behind as an insoluble white mass of hydrated dioxide, differing in many respects from that formed from the tetrachloride. Stannic hydroxide forms with strong bases salts of stannic acid,  $\text{H}_2\text{SnO}_3$ , which hydrolyze easily. Stannic acid is, therefore, a weak acid.



Hydrogen sulphide gives a yellow precipitate of stannic sulphide,  $\text{SnS}_2$ , with stannic solutions. The same compound can be prepared directly from tin and sulphur. It crystallizes in scales with a golden luster and is called "mosaic gold."

### § 43. GOLD.

**291. Gold.** — Gold occurs in Nature almost wholly in the free state, *i.e.*, as the uncombined element, and its purification, therefore, is based chiefly on mechanical methods of separation. The settling process, panning, which can be used to advantage because of the great density of gold, was for a long time the only method used in separating the costly metal from its ores.

As it became necessary to use material in which the gold is in such a fine state of subdivision that settling was no longer effective, various solution processes were developed. Mercury was used at first, as it dissolves the gold easily and freely and can be removed later by distillation. Other gold ores in which the gold was imbedded in quartz were made available by melting the quartz to a glass or slag, using a suitable flux, and in this way avoiding the difficult mechanical process of powdering so hard a substance. In very recent times gold-bearing masses have been found in South Africa in which the gold is so fine that it can be recovered only by chemical means. The details of this process cannot be considered here.

The properties of metallic gold are well known; it has a brilliant yellow color, density 19.3, high luster, and is wholly unchanged in the air, even at high temperatures and when sulphides are present. Pure gold is soft and tough. It can be drawn out to the finest wire and hammered to plates so thin that they begin to be transparent and look green by transmitted light. Gold leaf is used for covering objects of all sorts, and the gilding will last indefinitely unless removed by mechanical means.

For purposes of coinage and other practical uses, pure gold is not suitable because of its softness, so that it is generally alloyed with 10 per cent of copper, making it harder and giving it a redder shade. Silver makes gold lighter in color and in small amounts turns it green.

Gold is not soluble in nitric acid or in hydrochloric acid, but will dissolve in a mixture of the two acids which for this very reason has been called "aqua regia." The solvent action is due to the fact that the nitric acid oxidizes the hydrochloric acid, liberating chlorine which attacks the gold. Gold trichloride,  $\text{AuCl}_3$ , is formed as a brown salt, which dissolves in water forming a yellow solution. It combines with hydrochloric acid to form *chlorauric acid*,  $\text{HAuCl}_4$ , a monobasic acid the salts of which are used in photography for "toning." If the positive picture (p. 348), composed of brown metallic silver, is treated with a dilute gold solution, the latter is reduced by the silver with the formation of silver chloride. Metallic gold precipitates where the silver has been and gives the well-known violet tint to the picture. At the same time the picture becomes much more resistant to chemical action because of the "nobler" behavior of gold as compared to silver.

Other gold solutions are used in electroplating, which is based on exactly the same action as described in the electrical transference of copper from anode to cathode (p. 334). Metals can be plated in this way with gold layers of any desired thickness. The beautiful yellow color shows even with a very thin film.

#### § 44. PLATINUM.

**292. Platinum.** — Platinum, like gold, also occurs only in the free state, though often mixed with one or more of five other metals of similar character from which it has to be separated. The crude platinum ore, obtained by washing, is treated with aqua regia, which dissolves chiefly platinum. The addition of ammonium chloride (p. 248) to the acid solution throws down a yellow, crystalline precipitate having the composition  $(\text{NH}_4)_2\text{PtCl}_6$ , which, on heating, decomposes into ammonium chloride, chlorine, and platinum. The yellow compound is called ammonium chloroplatinate and is the ammonium salt of chloroplatinic acid, which has the composition  $\text{H}_2\text{PtCl}_6$ . Platinum is left behind, as it is very difficultly fusible, in the shape of a gray spongy mass, *platinum sponge*, the catalytic properties of which have been mentioned repeatedly.

Spongy platinum can be melted in the oxyhydrogen flame. It then flows together and forms an iron-gray, lustrous metal which melts at  $1770^{\circ}$  and has a density 21.4. It resembles gold in its resistance to chemical reagents and is, therefore, made into crucibles, dishes, etc., for laboratory use. It must be protected from free chlorine, but most other reagents do not attack it even on boiling. Molten caustic potash and caustic soda will attack it, however, although it is not affected by alkali carbonates. Phosphorus in the form of phosphates and in the presence of carbon or other reducing agents is very harmful to platinum vessels; phosphor-platinum forms easily and melts at a moderate temperature, so that crucibles sometimes become porous after heating with a compound of phosphorus. Carbon acts in the same way though much less strongly, so that it is always advisable to keep platinum apparatus from contact with smoky or reducing flames and to provide for a plentiful supply of air.

Because of its resistance to chemical action as well as its high melting point, platinum has been used in countless ways in the arts, and as the production is limited its price has increased rapidly in the last few years until to-day it is more valuable than gold. The catalytic uses of platinum have also led to an increased consumption.



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